

ปฏิริยาคาร์บอนไดออกไซด์รีฟอร์มมิงของมีเทนบนตัวเร่งปฏิริยานิกเกิล โคบอลต์บนตัว
รองรับอะลูมินาที่เตรียมโดยวิธีการโซลเจล



บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)
เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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ปีการศึกษา 2558
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

CO₂ reforming of methane on Al₂O₃-supported Ni,Co catalysts prepared by Sol-gel method

Mr. Supawat Pachop



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2015

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ศุภวรรษ พาชอบ : ปฏิกริยาคาร์บอนไดออกไซด์รีฟอร์มมิงของมีเทนบนตัวเร่งปฏิกริยานิกเกิล โคบอลต์บนตัวรองรับอะลูมินาที่เตรียมโดยวิธีการโซลเจล (CO₂ reforming of methane on Al₂O₃-supported Ni,Co catalysts prepared by Sol-gel method) อ. ที่ปริกษาวิทยานิพนธ์หลัก: ผศ. ดร.สุพจน์ พัฒนะศรี, 61 หน้า.

ซินแก๊สหรือแก๊สเชื้อเพลิงผสม เป็นผลิตภัณฑ์หลักจากปฏิกริยาคาร์บอนไดออกไซด์รีฟอร์มมิงของมีเทนซึ่งเป็นปฏิกริยาที่มีประสิทธิภาพในการเปลี่ยนแก๊สเรือนกระจกสองชนิดหลัก (CH₄ และ CO₂) ไปเป็นไฮโดรเจนและคาร์บอนมอนอกไซด์ด้วยอัตราส่วนระหว่างไฮโดรเจนต่อคาร์บอนมอนอกไซด์เท่ากับ 1 ในงานวิจัยนี้จึงเป็นการศึกษาตัวเร่งปฏิกริยาโลหะผสมบนตัวรองรับอะลูมินา โดยงานวิจัยนี้ศึกษาระหว่างโลหะ นิกเกิลและโคบอลต์เตรียมโดยวิธีการโซลเจล ซึ่งปัจจัยที่ศึกษาคือปริมาณอัตราส่วนระหว่างโลหะ นิกเกิลกับโคบอลต์ที่ถูกโหลดลงบนตัวรองรับที่ร้อยละโดยมวลจำกัดที่ร้อยละ 15 (7.5%Ni7.5%Co/Al₂O₃ หรือ 1Ni1Co/Al₂O₃, 10%Ni5%Co/Al₂O₃ หรือ 2Ni1Co/Al₂O₃ and 11.25%Ni3.75%Co/Al₂O₃ หรือ 3Ni1Co/Al₂O₃) โดยจะนำตัวเร่งปฏิกริยาที่มีอัตราส่วนที่เหมาะสมมาเปรียบเทียบระหว่างตัวเร่งปฏิกริยาในระบบโลหะเดี่ยว (Ni/Al₂O₃ และ Co/Al₂O₃) และโลหะผสมเป็นอีกปัจจัย การวิเคราะห์ลักษณะและคุณสมบัติของตัวเร่งปฏิกริยาทำโดย เทคนิค XRD, BET, SEM, NH₃, H₂-TPR, CO-CHEM และ TGA ปฏิกริยาคาร์บอนไดออกไซด์รีฟอร์มมิงของมีเทนดำเนินการที่อุณหภูมิ 700 องศาเซลเซียส อัตราส่วนคาร์บอนไดออกไซด์ต่อมีเทนเป็น 50:50 ตัวเร่งปฏิกริยาโลหะผสม 3Ni1Co/Al₂O₃ ให้ค่าร้อยละการเปลี่ยนของมีเทนและคาร์บอนไดออกไซด์สูงที่สุดซึ่งให้ค่าร้อยละการเปลี่ยนมีเทนเท่ากับ ร้อยละ 75 ค่าร้อยละการเลือกเกิดไฮโดรเจนที่ ร้อยละ 41 ค่าร้อยละการเลือกเกิดคาร์บอนมอนอกไซด์ที่ ร้อยละ 59 รวมถึงการกระจายตัว และพื้นที่ผิวมีค่าสูงถึงแม้ว่าจะมีปริมาณการเกิดโค้กมากกว่า ตัวเร่งปฏิกริยาอื่นแต่ก็อยู่ในปริมาณที่ยอมรับได้

ภาควิชา วิศวกรรมเคมี

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ปีการศึกษา 2558

5770471421 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: DRY REFORMING OF METHANE, SOL-GEL METHOD, BIMETALLIC CATALYST, NICKEL BASED CATALYST

SUPAWAT PACHOP: CO₂ reforming of methane on Al₂O₃-supported Ni,Co catalysts prepared by Sol-gel method. ADVISOR: ASST. PROF. SUPHOT PHATANASRI, Ph.D., 61 pp.

Syngas is a main product from dry reforming of methane (DRM) which is efficient reaction to convert two main greenhouse gases (CH₄ and CO₂) into hydrogen and carbon monoxide with H₂/CO ratio equal to 1. This study investigated the bimetallic NiCo on alumina-supported catalysts prepared by sol-gel method with different metal loading (7.5%Ni7.5%Co/Al₂O₃ or 1Ni1Co/Al₂O₃, 10%Ni5%Co/Al₂O₃ or 2Ni1Co/Al₂O₃, 11.25%Ni3.75%Co/Al₂O₃ or 3Ni1Co/Al₂O₃) and compared the optimal bimetallic catalyst with monometallic Ni/Al₂O₃ (15wt.%) and Co/Al₂O₃ (15wt.%). The synthesized catalysts were characterized by X-ray diffraction (XRD), N₂-physisorption, Scanning Electron Microscopy (SEM), NH₃ Temperature Programmed Desorption (NH₃-TPD), temperature programmed reduction (H₂-TPR), Thermo gravimetric analyze (TGA), and CO-chemisorption. The catalysts were used on DRM with composition of 50:50 (vol%) feed CH₄:CO₂ under atmospheric pressure at 700 °C. The bimetallic catalyst 3Ni1Co/Al₂O₃ exhibited the highest activities with H₂ selectivity of 41%, CH₄ conversion of 74%, CO conversion of 79%, high metal dispersion and high specific surface area. Moreover, the 3Ni1Co had high acceptable amount of carbon deposition and can be properly used for long term.

Department: Chemical Engineering Student's Signature

Field of Study: Chemical Engineering Advisor's Signature

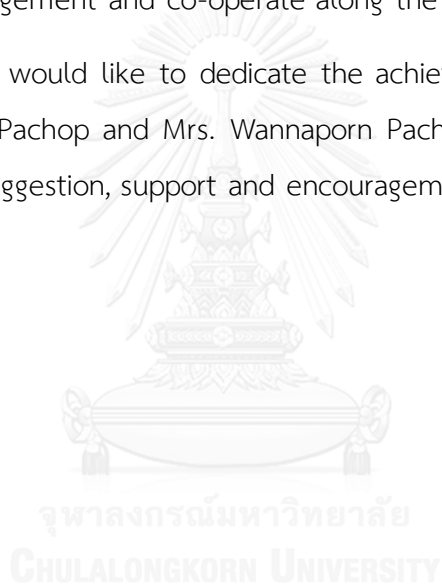
Academic Year: 2015

ACKNOWLEDGEMENTS

The author would like to gratefully acknowledge his advisor, Assistant Professor Suphot Phatanasri for his precious counsel, and valuable suggestions throughout this study. Without his guidance and persistent help this thesis would not have been possible.

Special thanks for kind suggestions and useful help to many friends in Center of Excellence on Catalysis and Catalytic Reaction Engineering who always provide the encouragement and co-operate along the thesis study.

Finally, she would like to dedicate the achievement of this work to her parents (Mr. Aroon Pachop and Mrs. Wannaporn Pachop) who have always been the source of her suggestion, support and encouragement.



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CHAPTER I

Introduction

1.1 MOTIVATION

The Earth's global average temperature is caused by: sunlight received, sunlight reflected and heat energy trapped and reradiated back to Earth by the atmosphere. The Earth has an atmosphere which contains certain gases which trap some of outgoing heat energy. These gases have the ability to absorb the heat energy radiated by the Earth and then reradiate it back to the surface. This process is called greenhouse effect and the cause of this phenomenon is greenhouse gases which included. It is necessary process for the Earth to maintain the temperature for the Earth surface of about 15 degrees C. Therefore, the Earth has excess greenhouse gases, surface temperature will reach higher than usual. It is more heat-trapping and it was oxidized capacity in the atmosphere than a molecule of CO₂. Carbon dioxide and Methane are the two main greenhouse gases. However, there are other important greenhouse gases in the atmosphere: nitrous oxide (N₂O), chlorofluorocarbons (CFCs), water vapor, and ozone (O₃). Carbon dioxide and methane come from both natural sources and human activities. CFCs are synthetic gases that were first manufactured in the 1940's and are used in many industrial products. Water vapor comes mainly from evaporation of oceans. The concentrations of all these gases in the atmosphere have increased in the 1800's.[1] And, most hydrogen is produced from fossil fuels in the world but mitigation of global warming is the growing concern with depletion of fossil fuel.[2] For this reason, new methods of H₂ production need to be developed. The new technologies were immediately improved to remove or convert methane and carbon dioxide to the renewable energy. Global warming leads to many problems that affect our environment.

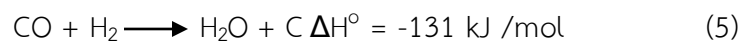
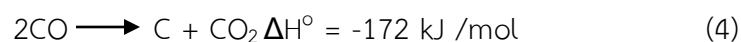
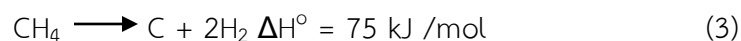
Currently, many industrial processes have been converted CO₂ and CH₄ to syngas. The dry methane reforming (DRM),(Eq. (1)) is a promising reaction for the simultaneous conversion of two major greenhouse gases to syngas with H₂/CO ratio equal to 1 and is thus suitable for the synthesis of oxygenated hydrocarbons and synthetic fuels.



It's normally accompanied by secondary reaction of the reverse water gas shift (Eq. (2))



However, the catalysts are suffered with big problem which is the carbon deposition by side reaction such as partial oxidation of methane Boudouard reaction and reverse carbon gasification are shown in Eq (3)-(5), respectively.[3, 4]



The main obstructive commercialization of this reaction is difficulty to find a catalyst with both high activity and stability. Catalysts that are active for the dry reforming of methane reaction is the noble metal based material (Ru > Rh > Pt > Pd).[5, 6] From a point of economy, high cost and low availability of noble metal caused the development of nickel-based catalyst more interesting which also prevent the coke formation.[7] The Ni particle size has a strong effect on the carbon tolerance of the catalyst, and generally, particles smaller than 5 nm have low catalytic activity towards the C - H cracking.[6] The Co/Al₂O₃ catalysts via sol-gel, impregnation and combination of sol-gel and impregnation methods. They illustrated, the sample prepared via sol-gel method demonstrated the better coking resistance than the other ones.[8] Ni and Co investigated in previous study of supported CeO₂ has shown higher activity and the presence of cobalt shows a substantially higher resistance to carbon deposition in comparison with Ni/ CeO₂ containing different Ni:Co ratios.[9, 10] Improvement of the preparing method of NiCo/Al₂O₃ from impregnation to sol-gel results in smaller Ni particle sizes, stronger metal-support and better activity.[11]

This study investigated the use of the Ni - Co/Al₂O₃, catalyst prepared by sol-gel method with different nickel and cobalt ratios loading. The loading ratios of nickel and cobalt indicate as followed 1:1, 2:1 and 3:1 by 15%wt of total metal loading, compared with monometallic catalysts: Ni/Al₂O₃ (15wt.%) and Co/Al₂O₃ (15wt.%). All catalysts were prepared by the incipient wetness impregnation method. The catalytic performances were tested in carbon dioxide reforming of methane.

1.2 Objective

1.2.1 To compare the catalytic performance of the bimetallic Ni – Co with the monometallic Ni catalyst and Co catalyst supported on Al_2O_3 . The catalysts were prepared by sol-gel method.

1.2.2 To compare the Ni:Co ratios loading of the bimetallic over dry reforming of methane reaction

1.3 Scopes of research

1.3.1 Preparation of the different loading order between cobalt and nickel metals supported on alumina which are prepared by sol – gel method

1.3.2 The selected metals loading order from the 1.3.1 are used to prepare the catalysts with different molar ratio of nickel and cobalt to obtain Ni:Co = 1:1 2:1 and 3:1. Total metal contents were fixed at 15 %wt. The monometallic catalysts are prepared at 15%wt Ni and 15%wt cobalt by sol-gel methods.

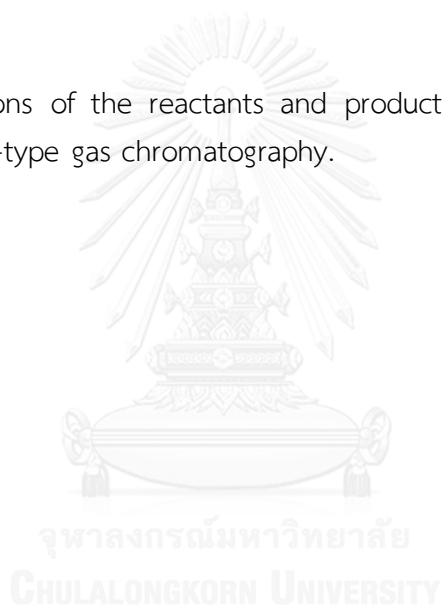
1.3.3 Characterization of chemical and physical properties of monometallic and bimetallic catalyst supported on $\gamma\text{-Al}_2\text{O}_3$ using various techniques:

- X-Ray diffraction pattern (XRD) was used to determine crystallite size and phase.
- Nitrogen adsorption-desorption was used to determine BET specific surface area, pore size and pore volume.
- Scanning Electron Microscopy (SEM) was used to study morphology.
- Ammonia temperature program desorption (NH_3 -TPD) was used to determine acidity of catalysts.
- Hydrogen temperature programmed reduction (H_2 -TPR) was used to determine the metal oxide reduction.
- Carbon monoxide chemisorption (CO-CHEM) was used to determine quantities of active site of catalysts.

- Thermogravimetric and differential thermal analysis (TG-DTA) was used to study carbon deposition.

1.3.4 Investigation of the catalytic performance of prepared catalysts via carbon dioxide reforming of methane reaction under the following condition:

- The catalysts were reduced in situ at 500 °C for 1 hr. in H₂ flow 50 ml/min.
- Reactant feed using the mixed gas between methane in carbon dioxide as ratio 1:1 was used with flow rate of 60 ml/min.
- The reaction was performed at the temperature of 700 °C at the atmospheric pressure.
- The gas compositions of the reactants and products were analyzed by thermal conductivity detector-type gas chromatography.



CHAPTER II

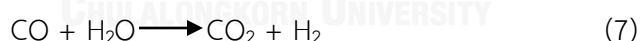
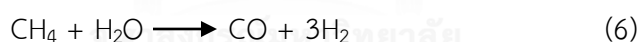
Theoretical and Literature review

2.1 Theoretical

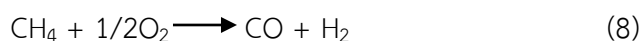
2.1.1 Syngas and Hydrogen production

Hydrogen is produced from many processes. The most of hydrogen is produced from fossil fuel. H₂ production is increasing because fossil fuels are being depleted. For this reason, new methods of H₂ production need to be developed. Produced syngas from several processed includes partial oxidation, steam reforming, dry reforming and oxy-reforming processes.[12]

- Steam methane reforming (SMR)[13] processes for the production of synthesis gas are Well known. The steam methane reforming process involves reacting a hydrocarbon feedstock (such as natural gas, refinery gas, or naphtha) with steam at elevated temperatures (up to about 900 °C.) and in the presence of a catalyst to produce a gas mixture primarily made up of hydrogen and carbon monoxide, commonly known as syngas. While syngas is used as a feed gas for multiple processes, the use of syngas for the production of hydrogen is the primary commercial application of the SMR process.

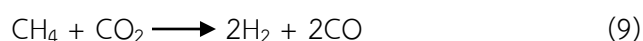


- Catalytic partial oxidation of methane (CPO) is an exothermic process and offers some benefits for the conversion of methane to syngas, such as short residence time, high conversion and selectivity[14] and CPO is an interesting alternative to the conventional steam methane reforming (SMR) for synthesis gas production.[15] It yields a suitable H₂/CO (about 2) ratio for the synthesis of methanol or dimethyl ether and for the Fischer–Tropsch synthesis. In addition, CPO can be operated in a millisecond contact-time reactor, making the process compact and thus suitable for on-board H₂ production in fuel cell applications.[16]



2.1.2 Carbon dioxide reforming of methane

Carbon dioxide reforming of methane (eq. (9)) (Dry reforming of methane, DRM) is an efficient way for the CH₄ and CO₂ valorization.[17] This process converts two greenhouse gases (CH₄ and CO₂) and produces syngas (H₂ and CO) with H₂:CO is around 1.[11] DRM is suitable for the synthesis of oxygenated chemicals and hydrocarbons from Fischer - Tropsch synthesis.



The syn- gas from dry reforming of methane have been regarded for transportation and storage solar energy.[18] Solar energy can convert methane and carbon dioxide to syn-gas that can be exported to places where energy sources are scarce. The energy stored in syn-gas is liberated by the back ward reaction and utilized as an energy source.[19] The application of the DRM for syn- gas production, the main prevention in industrial process by the following issues: (i) the reverse water gas shift reaction (RWGS) (eq. (10)) that, consuming H₂, lowers the H₂/CO ratio;



(ii) the catalyst deactivation and/or the reactor plugging due to carbon deposits formed by the methane cracking (Eq. (11)) and the Boudouard reaction (Eq. (12)).



The DRM is operated at high temperatures (generally above 923 K) to achieve suitable CH₄ and CO₂ conversions. In that condition, the Boudouard reaction is thermodynamically unfavoured, the RWGS is suppressed by the low CO₂ concentration, whereas, on the contrary, the methane cracking is favoured.[20] The tenor towards carbon deposition can be estimated by the ratio of O/C and H/C in the feed gas. The higher tendency towards carbon deposition will be observed in lower O/C and H/C ratio, which is the case in dry reforming of methane (CH₄/CO₂=1/1) having O/C=1 and H/C=2. Reverse case was observed for steam reforming of methane (CH₄/H₂O=1/1) having high O/C=1 and H/C=6. Similarly, partial oxidation of methane (CH₄/0.5 O₂) show edaquite higher ratio, O/C=1 and H/C=4. Considering the aforementioned ratios, it was clear that dry reforming of methane has a higher

tendency towards carbon deposition compared to steam reforming and partial oxidation of methane.[3]

2.1.3 Sol-gel method

The sol-gel process may be described as formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid. The idea of sol-gel synthesis is to dissolve the compound in a liquid in order to bring it back as a solid in a controlled manner.[21]

A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid, A gel consists of a three dimensional continuous network, which encloses a liquid phase. In a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles.[22] Generally, the sol particles may interact by van der Waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. The gelation process may be reversible if other interactions are involved.[23]

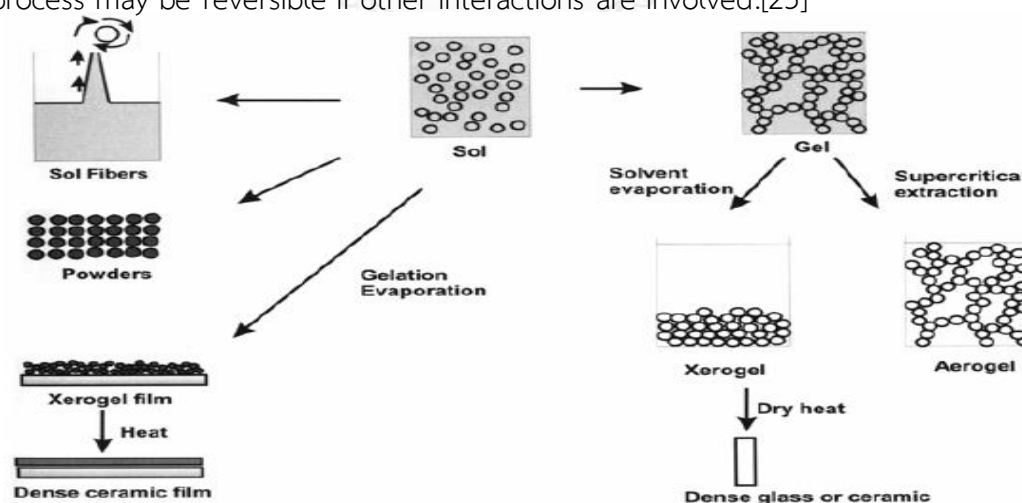


Figure 1.1 Sol-gel processing option

Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films. If the gel is dried by evaporation, then the capillary forces will result in shrinkage, the gel network will collapse, and a xerogel is formed. If drying is performed under supercritical conditions,

the network structure may be retained and a gel with large pores may be formed. This is called an aerogel, and the density will be very low.

2.1.4 Alumina

Alumina (Al_2O_3) or Aluminum Oxide is the only oxide formed by the metal aluminum and occurs in nature as the minerals corundum (Al_2O_3); diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$); gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$); and most commonly as bauxite, which is an impure form of gibbsite. The precious stones ruby and sapphire are composed of corundum (and thus also natural forms of alumina) getting their colors by small amounts of impurities.[24]

The structure of Aluminum Oxide has two types of sites, hexagonal and octahedral in which it holds the atoms. Hexagonal sites are the corner atoms in the cell while the octahedral sites are presented between two layers of vertical stacking. Aluminum cations are in 2/3 of the octahedral sites, and oxygen anions are in 1/3 of the octahedral sites. Each oxygen is shared between four octahedra. The oxygen presence in octahedral sites permits strong bonding and, therefore, gives rise to the characteristics of the properties of alumina. The type or structure of each alumina and its temperature range of existence are determined by the structure of the starting or precursor hydroxide; they are different for gibbsite, bayerite, nordstrandite, boehmite or diasporein. These seven aluminas are called "Transition Aluminas" and received Greek letters to identify them: gamma; delta; theta; kappa; chi; eta and rho. Figure 2.2 is adapted from the most recent review⁷ of the thermal transformation sequence: aluminum hydroxide transition aluminas $\alpha\text{-Al}_2\text{O}_3$ [25], and the physical and structural characteristics of important alumina phase formed at different calcinations temperatures are listed in Table 2.1.

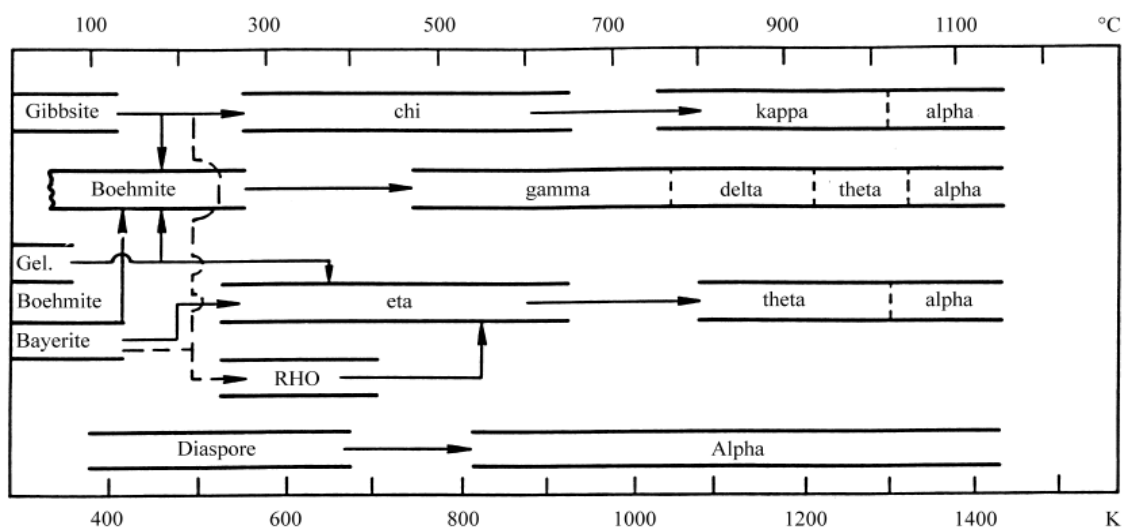


Figure 1.2 Alumina phase present at different temperatures[25]

Table 1.1 Physical and structural characteristic of common aluminum oxides.

$T_{\text{calc}}(^{\circ}\text{C})$	Alumina phase	SA (m^2/g)	$V_{\text{pore}}(\text{cm}^3/\text{g})$	$D_{\text{pore}}(\text{nm})$
250	pseudoboehmite	390	0.50	5.2
450	γ -alumina	335	0.53	6.4
650		226	0.55	9.8
850		167	0.58	14
950	δ -alumina	120	0.50	16.6
1050	θ -alumina	50	0.50	28
1200	α -alumina	1-5		

2.1.5 Metal catalyst

Nickel (Ni)[26]

Nickel is a silver-white metal that is used in a variety of industries. In our everyday lives, we are most likely to encounter nickel in coins and stainless steel products. Nickel is also an important part of many high-tech devices. Nickel is rarely found as a pure metal in nature. The element itself was only discovered in the eighteenth century. Instead, nickel is found in chemical compounds and minerals called ores. Nickel ores are often green or red.

Like all elements, individual nickel atoms are composed of even smaller particles. Most of an atom's mass is contained in a tiny nucleus at its center. The nucleus is made of particles called protons and neutrons. Protons have a positive electric charge. Neutrons have no charge but have the same mass as the protons. Smaller particles called electrons orbit the nucleus. They have almost no mass but a negative electric charge equal to a proton's positive charge. Atoms carry no overall electrical charge. The numbers of electrons and protons in an atom are always equal and their charges are canceled out. In nickel, 28 protons are held in the nucleus and 28 electrons orbit around them. Each element has a unique number of protons or electrons. This is called its atomic number. Nickel's atomic number is 28. Most nickel compounds are blue or green. Nickel dissolves slowly in dilute acids but like iron, becomes passive when treated with nitric acid. Finely divided nickel adsorbs hydrogen.

Physical Properties

From Table 2 shows the physical property of cobalt

Table 1.2 Physical properties of Nickel.

Parameters	Value
Name	Nickel
Symbol	Ni
Atomic number	28
Atomic mass	58.71 g.mol ⁻¹
Electronegativity according to Pauling	1.8
Density	8.9 g.cm ⁻³ at 20°C
Melting point	1453°C
Boiling point	2913°C
Vanderwaals radius	0.124 nm
Ionic radius	0.069 nm (+2) ; 0.06 nm (+3)
Isotopes	10

Cobalt[27]

Cobalt-based catalyst began to be widely studied for the carbon dioxide reforming of methane because had good activity availability and low cost. Cobalt is one of life's essential elements, at least for humans and animals. We could not survive without it. Like twenty-six other elements, cobalt is a necessary part of our bodies. Cobalt is the central atom in each molecule of vitamin B₁₂, which is an important substance that we get in our food. Vitamin B₁₂ helps the body make blood. Cobalt has plenty of other uses. The most familiar use is probably as a coloring material for glass and pottery. For example, adding cobalt oxide to glass produces a deep blue color.

Cobalt itself is a metal, with a shiny, blue-silver appearance. Like other elements, atoms of cobalt are made up of three types of tiny particles: protons and neutrons in the nucleus (center) of each atom, and electron orbiting the nucleus. A proton has a positive charge. Neutrons have no charge at all – they are neutral. The atomic number is the number of protons in an atom. Atoms have no overall charge so there is always the same number of electrons as protons in an atom. Cobalt's atomic number is 27, which means that all cobalt atoms have 27 protons and 27 electrons. Cobalt compounds are used in chemical reactions such as cobalt acetate is used for the convert of xylene to terephthalic acid, the precursor to the bulk polymer polyethylene terephthalate. Moreover, cobalt is also a catalyst in the Fischer–Tropsch reaction, used in the hydrogenation of carbon monoxide into liquid fuels.

Physical Properties

From Table 3 shows the physical property of cobalt

Table 1.3 Physical properties of cobalt

Parameters	Value
Name	Cobalt
Symbol	Co
Atomic number	27
Element category	Transition metal
Atomic weight	58.93
Electronegativity	1.88 (Pauling scale)
Ionization energies, Kj.mol^{-1}	
1 st	760.4
2 nd	1648
3 rd	3232
Latent heat of fusion	395
Boiling point	3100
Latent heat of vaporization at bp, ΔH_{vap}	6276
kJ/g^{a}	
Specific heat, $\text{J}/(\text{g}.\text{°C})^{\text{a}}$, 15-100 $^{\circ}\text{C}$	
- Molten metal	0.442
Coefficient of thermal expansion, $^{\circ}\text{C}^{-1}$	0.560
- Cph at room temperature	12.5
- Fcc at 417 $^{\circ}\text{C}$	14.2

2.2 Effect of Preparation

S. M. Sajjadi and et al. (2013)[7] studies the influence of the preparation method on catalytic activity of the Ni/Al₂O₃ nanocatalysts which were prepared via sol-gel and impregnation methods. And they discuss the efficiency of loading of Co and Cu as active phase with constant quantity over the catalytic performance of the nanocatalysts. The Ni - Co and Ni - Cu are prepared with approximately 15%Ni5%Co/Al₂O₃, 15%Ni5%Cu/Al₂O₃ and 15%Ni/Al₂O₃. The sol-gel samples show higher surface area and higher vibration of -OH bonds on the surface of sol-gel prepared samples which were improved the basicity of catalysts and subsequently enhanced the CO₂ adsorption. The effect of synergetic Co promoter and sol-gel method depict excellent characterization such as higher surface area and smaller particle size by improving the formation of the crystalline Al₂O₃. In conclusion, The Ni - Co/ Al₂O₃ sol-gel sample highly presents performance for DRM and good characteristics.

M. Sharifi and et al. (2014)[28] studies the effect of synthesis method (impregnation and sol-gel) and Co and Cu addition over catalytic performance of Ni/Al₂O₃ - ZrO₂. NiCo/Al₂O₃ - ZrO₂ has the excellent activity and selectivity. The catalysts are prepared with (10%wt) Ni/ Al₂O₃ - ZrO₂ (10%wt), (10%wt) Ni (3%wt) Co, Cu/ Al₂O₃ - ZrO₂ (10%wt). The researcher found the application of ZrO₂ as promoter and the sol-gel method is suitable to synthesis catalyst. Co addition encourages activity of Ni for CH₄ decomposition and CO₂ dissociation. And Cu addition has no suitable effect on the nanocatalyst activity in the approximately whole reaction temperature range. This behavior can be explained by the higher carbon deposition content.

I. Luisetto et al. (2015)[20] studies Ni/CeO₂-Al₂O₃ catalysts with different crystallite size and Ce³⁺/Ce⁴⁺ ratio. Catalysts are prepared co-precipitation, wet impregnation, sol-gel and citric acid methods with 10% wt Ni and 20% wt CeO₂ supported on Al₂O₃. Sol-gel sample shows NiO peak with the highest intensity. The citric acid method shows particularly attractive with very small Ni crystallite size and high CeAlO₃ content which benefit role in increasing the rate of carbon gasification. The Co-precipitation and Citric acid methods are the most active catalysts during time on

stream and the citric acid method results comparable performances with minor carbon deposition, shows suitable catalyst for long term operation.

2.3 Effect of support and metal

I. Luisetto et al. (2012)[9] investigates the effect of Co loading over Ni based catalyst supported on CeO_2 and compares with monometallin (Ni/CeO_2 and Co/CeO_2). The catalyst samples are prepared surfactant assisted co - precipitation method. The metal loadings are 7.5 %wt Co in Co/CeO_2 , 7.5 %wt Ni in Ni/CeO_2 , 3.75 %wt Co and 3.75 %wt Ni in $\text{Co} - \text{Ni}/\text{CeO}_2$. The bimetallic catalyst improves the specific area, metal dispersion and high intensity of NiO which activates in DRM reaction. Both cobalt containing catalysts (Co/CeO_2 and $\text{Ni} - \text{Co}/\text{CeO}_2$) show higher resistance carbon deposition in comparison with Ni/CeO_2 , clearly showing that cobalt is effective in preventing in carbon deposition. Bimetallic is a promising system because it is high activity and high resistance the cause of deactivation, high selectivity and thermal stable catalyst for syngas production by DRM.

K. Takanabe et al. (2005)[6] studies to compared combine the pure cobalt, pure nickel and to suppress both metal oxidation and carbon formation. Catalyst with various Co/Ni ratios have been prepared and tested over CO_2 reforming of methane. $\text{Co} - \text{Ni}/\text{TiO}_2$ were prepared by incipient wetness co - impregnation with metal loading 10 wt% in total. $\text{CoNi} (90:10)/\text{TiO}_2$ showed much higher and more stable activity (CH_4 conversion 34%). The catalytic activity increased gradually with increasing Ni content. The $\text{Co} - \text{Ni} (10:90)/\text{TiO}_2$ and Ni/TiO_2 catalysts showed slightly higher TOFs. In conclusion, the small nickel substitution of cobalt (10 mol%) dramatically improved the catalytic activity and stability.

S. Senghuta et al. (2014)[29] studies the effect of modifying $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst with cobalt on the dry reforming of methane and cracking of methane reactions. The catalysts are prepared by Incipient Wetness Impregnation (IWI) technique and the Ni:Co ratio in $\text{Ni} - \text{Co}/\text{Al}_2\text{O}_3$ catalyst was varied. The alumina supported Ni and Co catalysts containing 15wt% metal are referred to as $15\text{Ni}/\text{Al}_2\text{O}_3$ and $15\text{Co}/\text{Al}_2\text{O}_3$, respectively. Depending on the Ni and Co percent the $\text{Ni} - \text{Co}/\text{Al}_2\text{O}_3$ catalysts are referred to as:

75Ni25Co/Al₂O₃, 50Ni50Co/Al₂O₃ and 25Ni75Co/Al₂O₃. The 75Ni25Co/Al₂O₃ catalyst shows high initial activity and slight drop remain relatively constant for 3 h. The TOF of dry reforming of methane of 75Ni25Co/Al₂O₃ catalysts is greater than 15Ni/Al₂O₃ and other Ni - Co/Al₂O₃ catalysts. Also, 75Ni25Co/Al₂O₃ catalyst is the highest CH₄ conversion, followed by 15Ni/Al₂O₃ and the other catalysts in cracking of methane reaction.

E. G. Mahoney et al. (2014)[2] studies the effect of Pt addition to supported Ni catalysts on dry reforming of methane to syngas. Pt - Ni/CeZrO₂ catalyst compares with Pt - Ni/Al₂O₃ catalyst and monometallic for dry reforming of methane at different temperature. The bimetallic catalysts are prepared by sequential impregnation with 15%wt Ni and 0.2%wt Pt and Monometallic catalysts (Ni/Al₂O₃ and Ni/CeZrO₂) are prepared by incipient wetness impregnation method with 15%wt of Ni. The addition of Pt to Ni does not change the methane and CO₂ conversions significantly during dry reforming reaction of methane. Both the alumina supported catalysts are higher the H₂:CO ratios than the CeZrO₂ supported catalysts. The results of reaction studies show the presence of Pt enhances the reducibility of the bimetallic catalysts and makes them better catalysts for H₂ production at moderate temperature.

J. Min et al (2015)[11] studies the effect of Mg/Al ratios on carbon dioxide reforming of methane on Ni - Mg - Al₂O₃ prepared by sol-gel method and co - precipitation. The Ni content is fixed at 15%wt. MgO/(MgO + Al₂O₃) includes 0, 0.06, 0.14, 0.28, 0.44, 0.61, 0.76, 0.86, 0.94, and 1. The sol-gel provides more efficient preparation for dispersion of nickel particles in the Ni - Mg - Al₂O₃ showing in better resistance to coke formation in DRM than co-precipitation among the catalysts prepared by sol-gel method. Ni - Al₂O₃ shows poor activity and stability due to the formation of structure of NiAl₂O₄. Basic property of MgO improves Ni catalysts to have enhanced resistance to coke formation. The dropping mixing of alumina and magnesium oxide matrix for nickel catalysts leads to improve activity with high stability remaining to high surface area and Ni dispersion are promoted by Al₂O₃. MgO/(MgO + Al₂O₃) ratio of 0.44–0.86 has the higher catalytic performance.

CHAPTER III

EXPERIMENTAL

In this chapter consist of three sections involved in the preparation process of catalyst. First, prepare for alumina and loaded metal Ni and Co mixed with alumina by sol-gel method.

The catalyst are prepared with various molar ratio (Ni:Co = 1:1, 2:1 and 3:1) and fixed total metal for 15%wt. Second, characterize physical properties of mono metallic and bimetallic catalyst supported on Al₂O₃ by using various techniques: X-Ray diffraction pattern (XRD), Nitrogen adsorption-desorption, Scanning Electron Microscopy (SEM-EDX), Hydrogen temperature program desorption (H₂-TPR), Carbon monoxide chemisorption and Thermogravimetric and differential thermal analysis (TG-DTA). Last, investigate performance of catalysts for carbon dioxide reforming of methane reaction.

3.1 Catalyst preparation

3.1.1 Catalyst by sol-gel method

- Alumina mixed with different metal loading by sol-gel method.

Chemical of alumina

- a) Alumina Isopropoxide: AIP, $[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$ from Aldrich.
- b) Ethanol, (C₂H₅OH) from Merck
- c) Hydrochloric acid, (HCl) from Merck

- Nickel and Cobalt - base metal catalyst

Chemicals of nickel metal

- a) Nickel nitrate hexahydrate, $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ from Carlo Erba

Chemicals of cobalt metal

- b) Cobalt nitrate hexahydrate, $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ from Carlo Erba

Preparation of nickel and cobalt – base metal loading on alumina support by sol-gel method

The precursor, alumina isopropoxide dissolved in mixture of ethanol and deionized water with volume ratio 1:1 under mild stirring at 80 °C for 1 hr. Then, the nickel and cobalt were mixed into the solutions with 15%wt Ni and 15%wt Co. Then,

hydrochloric acid was dropped into the solutions until pH value is equal to 2.5 and aged with stirring at 80 °C about 5 hr. After that, the catalysts were dried at 105 °C overnight and calcination at 500 °C for 2 hr.

- Bimetallic catalysts

Chemicals of bimetallic

a) Nickel nitrate hexahydrate, $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ from Merck

b) Cobalt nitrate hexahydrate, $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ from Carlo Erba

Preparation of Ni-Co bimetallic catalysts loaded on alumina support by sol-gel method.

The bimetallic catalyst Ni – Co are loaded on alumina with various Ni:Co ratios (1:1, 2:1, and 3:1 with fixed total 15%wt content) are prepared by the sol-gel method and aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of the appropriate concentration to have the metal loading above. The gel was dried at 105 °C overnight and calcination under air at 500 °C for 2 hr.

3.2 Catalyst characterization

3.2.1 X-ray diffraction (XRD)

The analysis of crystalline phases is performed by X-ray diffraction (XRD) patterns of the samples are carried on an X-ray diffraction SIEMENS D 5000 connected to a personal computer with Diffract AT version 3.3 program for fully control of XRD analyzer. The XRD analysis is conducted to Cu-K α radiation between 20° - 80° with a generator voltage and current of 30 kV and 30 mA, respectively.

3.2.2 Nitrogen adsorption-desorption

The catalyst 0.1 gram are study BET surface area, pore volume and pore diameter are measured by N₂ adsorption–desorption isotherm at liquid nitrogen temperature (-196 °C) using a Micromeritics ASAP 2020. The surface area and pore distribution are calculated according to Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods.

3.2.3 Scanning Electron Microscopy (SEM-EDX)

Scanning Electron Microscopy is employed for including morphology metal dispersion of catalysts. The JEOL JSM-35 CF model at the Scientific and Technology Research Equipment Centre, Chulalongkorn University (STREC) was used for this purpose.

3.2.4 Ammonia temperature program desorption (NH₃-TPD)

The acid properties of prepared catalysts are observed by Temperature Programmed Adsorption of Ammonia (NH₃-TPD) equipment by using Micromeritics chemisorp 2750 Pulse Chemisorption System. In an experiment, 0.10 g of the catalyst sample is placed in a quartz tube and pretreated at 200 °C in a flow of helium. The sample was saturated with 15% NH₃/He. After saturation, the physisorbed ammonia was desorbed in a helium gas flow about 30 min. Then the sample was heated from 40 to 500 °C at a heating rate 10 °C/min. The amount of ammonia in effluent was measured via TCD signal as a function of temperature.

3.2.5 Thermogravimetric analysis (TGA)

The as-spun alumina fibers were subjected to the thermogravimetric and differential thermal analysis (Diamond Thermogravimetric and Differential Analyzer, TA Instruments SDT Q600) to determine the carbon content in the sample, as well as their thermal behaviors in the range of room temperature to 1000 °C. The analysis was performed at a heating rate of 10 °C/min in 100 mL/min flow air.

3.2.6 Hydrogen temperature programmed reduction (H₂-TPR)

The reducing temperatures of prepared catalysts are observed by Temperature Programmed Reduction of Hydrogen (H₂-TPR) equipment by using Micromeritics chemisorp 2750 Pulse Chemisorption System. In an experiment, about 0.10 g of the catalyst sample is placed in a quartz tube and pretreated at 200 °C in a flow of nitrogen. The sample is reduced with 10% H₂/Ar. Then the sample is heated from 30 to 800 °C at a heating rate 10 °C/min. The amount of hydrogen consumption in effluent is measured via TCD signal as a function of temperature.

3.2.7 Carbon monoxide chemisorption

Static CO chemisorption at room temperature on the reduce catalysts will be used to determine the number of reduce surface nickel and cobalt metal atoms. The total CO chemisorption will be calculated from the number of injection of a known

volume. CO chemisorption will be carried out following the procedure using a Micrometrics chemisorb 2750 Pulse Chemisorption System. In an experiment, about 0.10 g of the catalyst sample is placed in a quartz tube. Prior to chemisorption, the catalysts will be reduced at 500 °C for 1 hour after ramping up at a rate of 10 °C/min. After that, carbon monoxide 20 microliter was injected to catalyst and repeat until desorption peak constant. Amount of carbon monoxide adsorption on catalyst was relative amount of active site

3.3 Reaction in carbon dioxide reforming of methane

3.3.1 Material

In this reaction, the CH₄ in CO₂ feed was used to the reactant gas from Thai Industrial Gas Limited (TIG). The carbon dioxide reforming of methane was operated using 0.2 g catalyst packed in a fixed-bed continuous-flow quartz reactor feed mixture composition of CH₄:CO₂ 50:50 Vol% the total gas flow rate was 60 ml/min. The catalyst was heat from ambient temperature to 600 °C and reduced in flowing H₂ for 1h under atmospheric pressure. Then, the synthesized catalysts were tested in dry methane reforming reaction (DRM) at 700 °C. The exit gas was analyzed by Thermal Conductivity Detector-type gas chromatograph (Shimudzu, GC-8A) equipped with Porapak-Q and Molecular sieve 5A packed column.

3.3.2 Apparatus

The dry reforming of methane are tested in flow system as shown in Figure 3.1. The apparatus included of a fixed-bed continuous-flow quartz reactor, electrical furnace and temperature controller. The instruments used in this system are listed and explain flow;

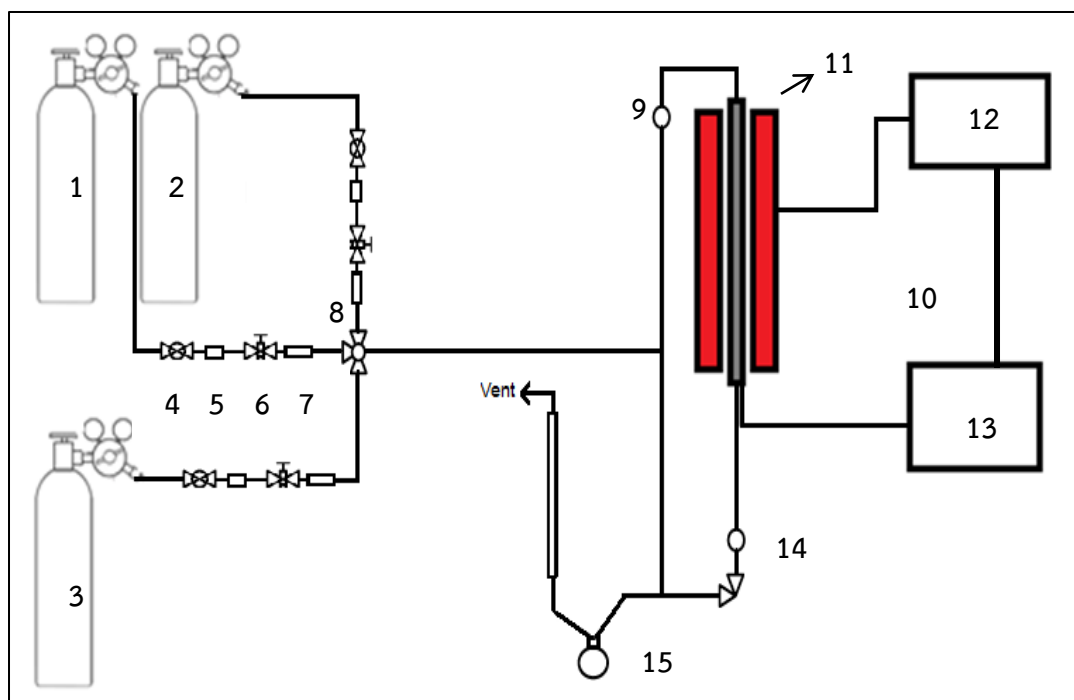


Figure 3.1 Flow Diagram of carbon dioxide reforming of methane.

- | | |
|---|----------------------------------|
| 1. H ₂ gas cylinder | 9. Inlet gas inject port |
| 2. N ₂ gas cylinder | 10. Furnace |
| 3. CH ₄ :CO ₂ balance gas (1:1 ratio) | 11. Quartz tube |
| 4. On-off valve | 12. Temperature controller |
| 5. Filter | 13. Variable voltage transformer |
| 6. Mass flow controller | 14. Outlet gas inject port |
| 7. Check valve | 15. Bubble flow |

3.3.2.1 Reactor

The reactor was a quartz tube. Length of 47 mm and inner diameter of 12 mm. The catalyst was filled between quartz wool layers.

3.3.2.2 Temperature controller

There is a magnetic switch connected to a variable voltage transformer and a temperature controller this system included a thermocouple attached to the catalyst bed in reactor. A dial setting established a set point at any temperature within the ranged between 0 °C to 1000 °C.

3.3.2.3 Electrical furnace

This supply required heated to the reactor for reaction. The reactor could be operated at 700 °C

3.3.2.4 Gas controlling system

Gas was adjusted by a pressure regulator (0-120 psig), an on-off valve and needle valve were applied adjust flow of gas.

3.3.2.5 Gas chromatographs

Gas composition in feed and product were analyzed by a Shimadzu GC8A gas chromatograph equipped with a TCD (Thermal conductivity detector). The operating conditions for each instrument are summarized in Table 3.1.

Table 3.1 Operating condition of gas chromatograph in carbon dioxide reforming of methane

Gas Chromatograph	Shimadzu, GC-8A	
Detector	TCD	TCD
Column	Porapack-Q	Molecular sieve 5A
Carrier gas	Ar	Ar
Carrier gas flow	50 ml/min	50 ml/min
Column temperature		
-Initial	70°C	70°C
-Final	70°C	70°C
Detector temperature	100°C	100°C
Injector temperature	100°C	100°C
Current (mA)	80	80
Analyzed gas	CO ₂	H ₂ , CH ₄ , CO

3.3.3 Reaction method

The carbon dioxide reforming of methane was carried out at atmospheric pressure in fix-bed flow reactor (quartz tube, inner diameter 12 mm and length 47 mm) packed with 0.05 g catalyst and quartz wool for 0.1 g. The reactor temperature was measured and controlled by K-type thermocouple positioned at the middle of catalyst bed. The catalyst was reduced in pure hydrogen (50ml/min) at 600°C for 1 h. Then, the hydrogen was replaced by pure nitrogen (50ml/min) and the system was heated (10°C/min) to the reaction temperature for 30 min. The catalytic performance test was carried out at 700°C. The feed gas consisted of methane and carbon dioxide (volume ratio 1:1), and feed flow rate 75 ml/min. The gas compositions of reactants and products were analyzed by TCD detector type gas chromatograph (Shimadzu, GC-8A) equipped with a Porapack-Q and Molecular sieve 5A packed column.

CHAPTER IV

Results and Discussion

There are two parts in this chapter. Firstly, 4.1 studies of different loading ratios between nickel and cobalt metals to obtain 7.5%wt.Ni7.5%wt.Co/Al₂O₃ (1Ni:1Co), 10%wt.Ni5%wt.Co/Al₂O₃ (2Ni:1Co), 11.25%wt.Ni3.75%wt.Co/Al₂O₃ (3Ni:1Co). Secondly, 4.2 studies the comparison of bimetallic catalysts and monometallic catalysts (15%Ni/Al₂O₃, 15%Co/Al₂O₃). Either section explains catalyst characterization by various techniques such as X-Ray diffraction pattern (XRD), nitrogen adsorption-desorption, Hydrogen temperature programmed reduction (H₂-TPR), Ammonia temperature program desorption (NH₃-TPD), scanning electron microscopy (SEM-EDX), carbon monoxide chemisorption, thermo gravimetric and differential thermal analysis (TG-DTA) and catalytic activities and selectivity in carbon dioxide reforming of methane reaction.

4.1 Study the comparison between monometallic and bimetallic catalyst.

4.1.1 Characterization of catalyst

4.1.1.1 X-Ray Diffraction

There are XRD pattern of the the γ -Al₂O₃ in Fig. 4.1 and XRD pattern of the catalysts to obtain 15%wt.Ni/ γ -Al₂O₃, 7.5%wt.Ni7.5%wt.Co/ γ -Al₂O₃ (1Ni:1Co) and 15%wt.Co/ γ -Al₂O₃ indicated in Fig. 4.2. The catalysts were prepared by sol-gel method. And then, there was calcined at 500°C. The XRD patterns of γ -Al₂O₃ were shown at 39.3°, 45.6° and 66.6°. The XRD patterns of 15%wt.Co/Al₂O₃ were shown at 37.2°, 37.4°, 44.9°, 45.1, 59.4, 59.6°, 65.6°, and 65.7° which ascribed to CoO or Co₃O₄. the XRD patterns of 15%wt.Ni/Al₂O₃ were shown peak of NiO or NiAl₂O₄ at 37.1°, 37.2°, 43.4°, 45.2°, 63.1°, and 65.7°[2]. The CoO, Co₃O₄, NiO and NiAl₂O₄ have no significant different which suggests that those may have similar morphology.

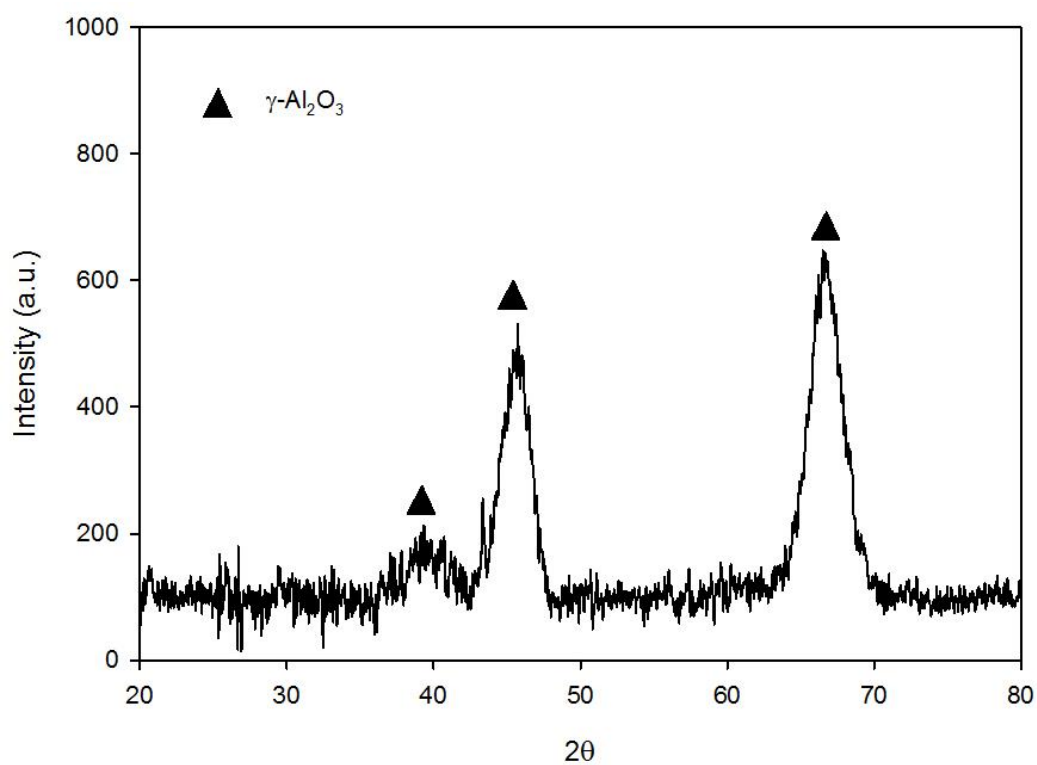


Figure 4.1 XRD pattern of $\gamma\text{-Al}_2\text{O}_3$.

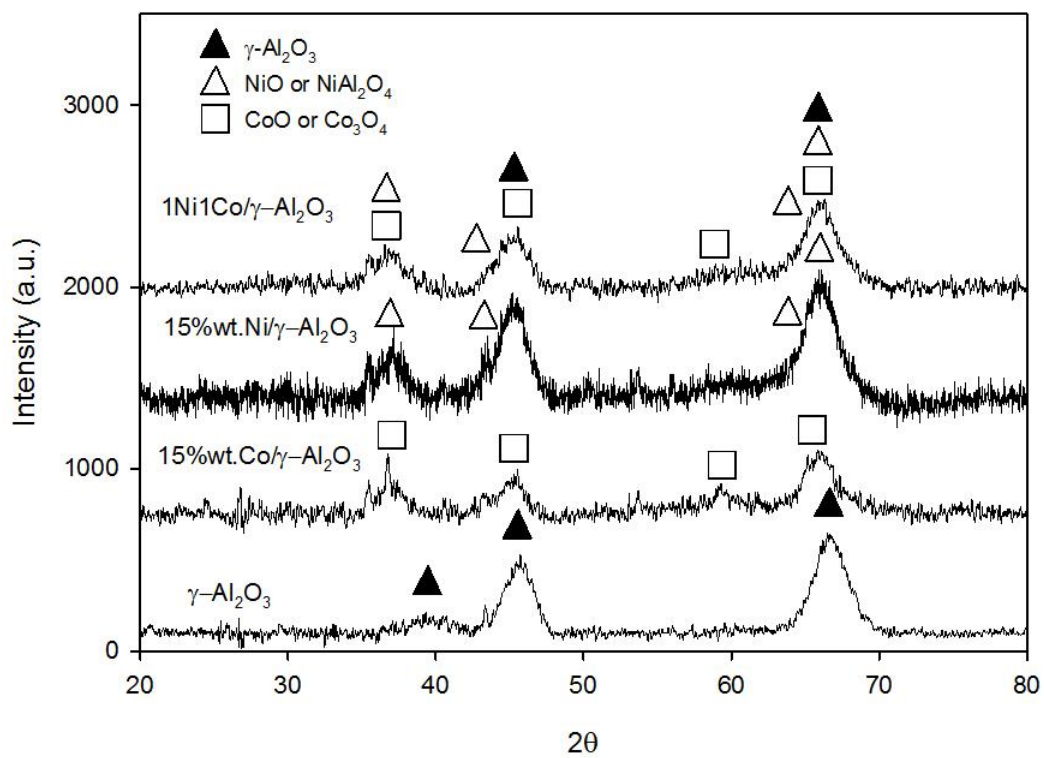


Figure 4.2 XRD pattern of monometallic catalysts, bimetallic catalyst and support.

4.1.1.2 Nitrogen adsorption-desorption

The specific surface areas of calcined support and the different bimetallic loading content catalysts were measured using the Brunauer-Emmitt-Teller Method (BET). BET surface area, pore volume, and pore size of monometallic Ni, Co catalysts and bimetallic 1Ni1Co on Al_2O_3 catalysts were summarized in Table 4.1. For mono metallic and bimetallic have specific surface area 146- 189 m^2/g . The surface areas of bimetallic catalyst (1Ni1Co/ $\gamma\text{-Al}_2\text{O}_3$) were slightly less than the 15%wt.Ni catalysts and also all catalyst were less surface area than alumina. This suggests that the loaded Ni and Co metal particle may blocked some pore of alumina support.

Table 4.1 BET surface areas, pore volume, pore size and dispersion of monometallic and bimetallic on $\gamma\text{-Al}_2\text{O}_3$ catalysts.

Catalyst	BET surface area (m^2/g)	Average pore diameter (nm) ^a	Pore volume (cm^3 (STP)/g) ^a
$\gamma\text{-Al}_2\text{O}_3$	189	2.9	0.2
15%wt.Ni/ $\gamma\text{-Al}_2\text{O}_3$	187	3.3	0.22
1Ni1Co/ $\gamma\text{-Al}_2\text{O}_3$	176	3.1	0.21
15%wt.Co/ $\gamma\text{-Al}_2\text{O}_3$	146	3.2	0.19

^aCalculated from BJH model.

The N_2 adsorption-desorption isotherm of $\gamma\text{-Al}_2\text{O}_3$ and the catalysts are showed in Fig. 4.3 and Fig. 4.4. All samples can be classified as a type IV which attributed for micro-mesoporous materials and all samples were assigned to the H2 type adsorption hysteresis is involved with a consequence of the interconnectivity of pores.

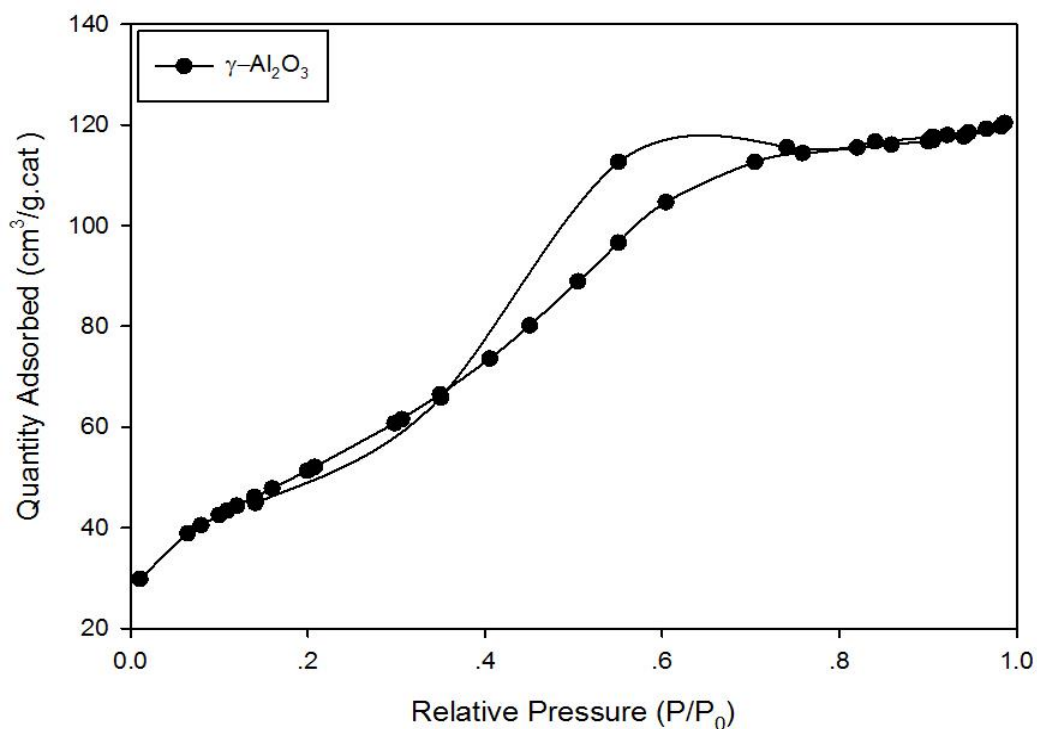


Figure 4.3 The nitrogen adsorption/desorption isotherms of support.

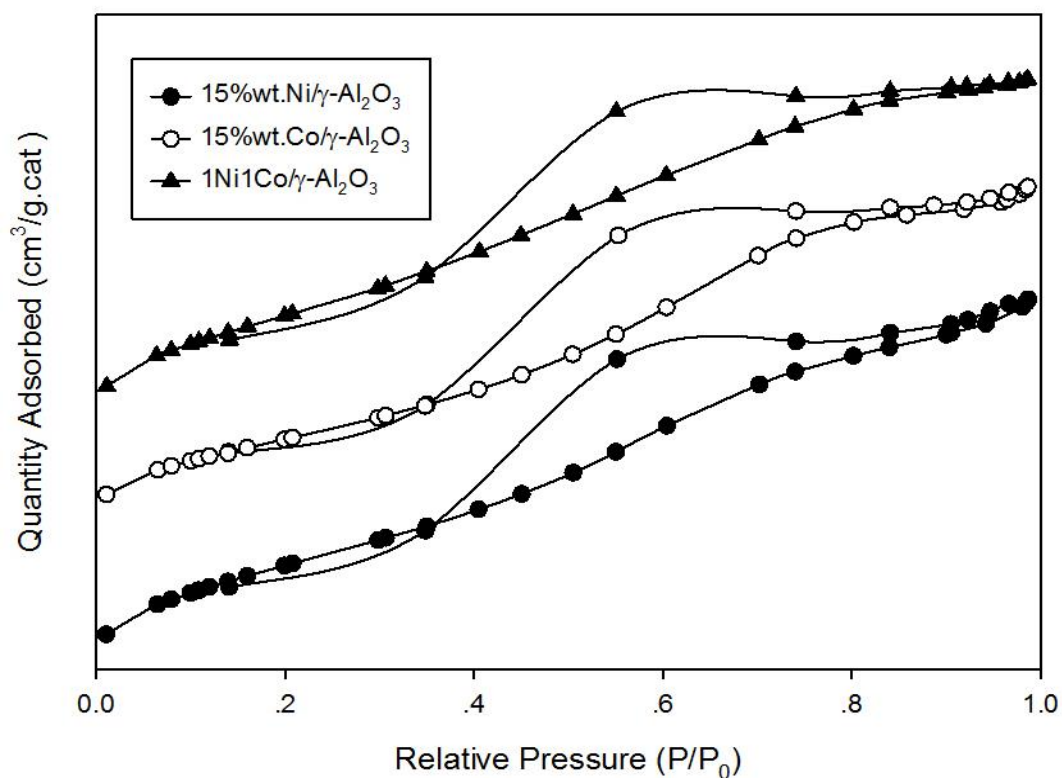


Figure 4.4 The nitrogen adsorption/desorption isotherms of monometallic and bimetallic catalyst.

4.1.1.3 Scanning Electron Microscopy (SEM-EDX)

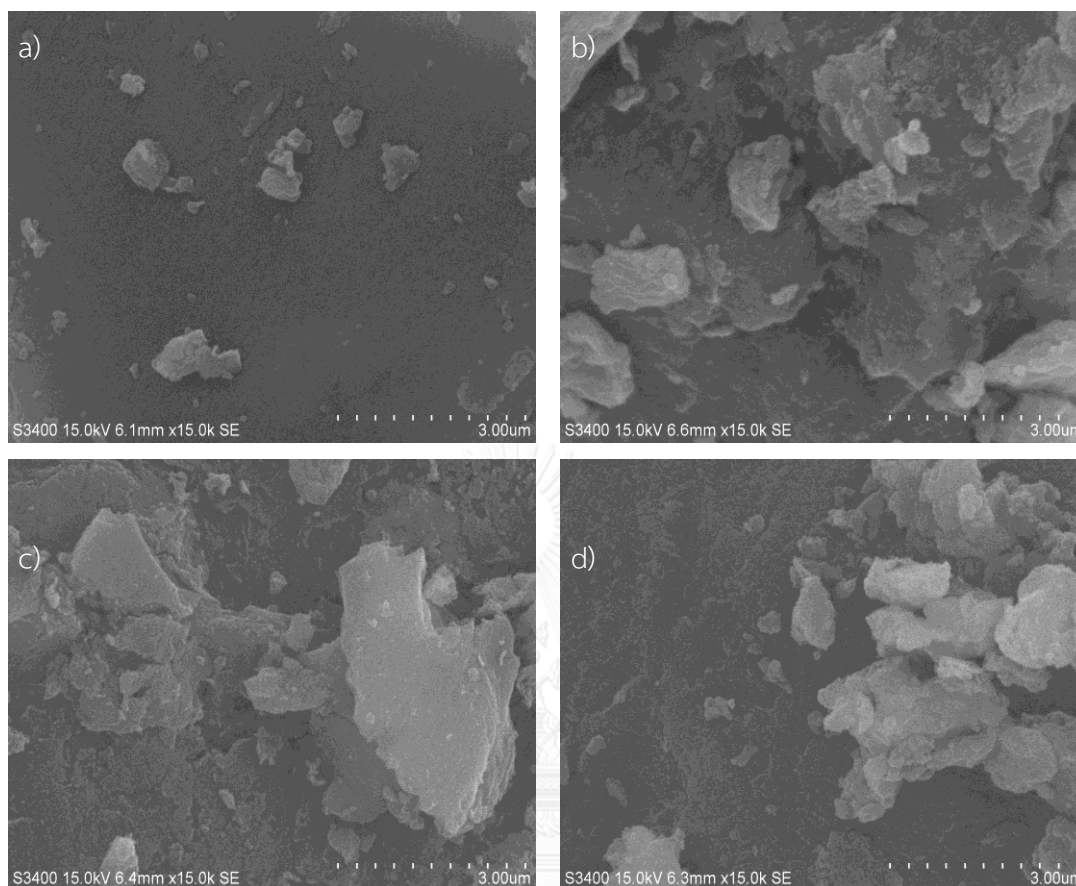


Figure 4.5 The SEM images of the a) γ - Al_2O_3 , b) 1Ni1Co/ γ - Al_2O_3 , c) 15%wt.Co/ γ - Al_2O_3 , and d) 15%wt.Ni/ γ - Al_2O_3 .

The morphology of γ - Al_2O_3 , 1Ni1Co/ γ - Al_2O_3 , 15% wt. Co/ γ - Al_2O_3 and 15%wt.Ni/ γ - Al_2O_3 were shown in Fig. 4.5. The bimetallic catalyst image shows that the crystallinity of the supports which suggests that is not affected by NiO and CoO loading. Moreover, the monometallic catalyst might agglomerate with the excess loading metal which could affect activities of catalyst[30].

4.1.1.4 Hydrogen temperature program reduction (H_2 -TPR)

The TPR profiles of monometallic catalysts and bimetallic catalyst was shown in Fig. 4.6.

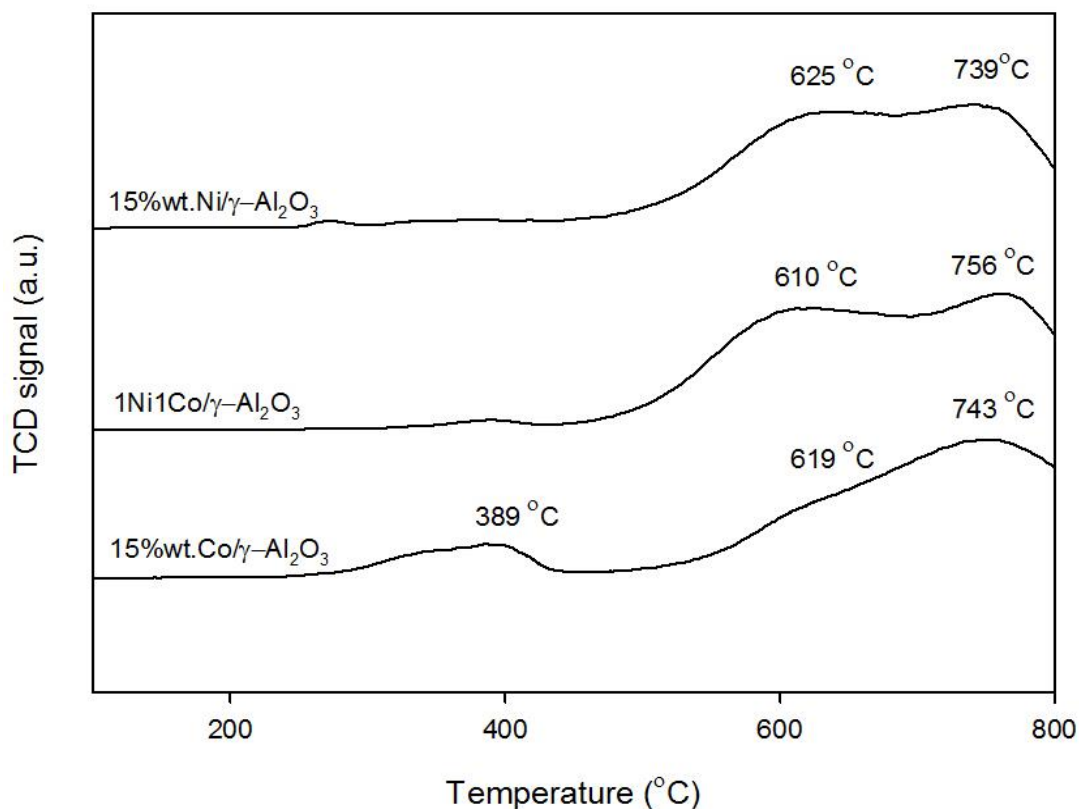


Figure 4.6 The TPR profiles of the monometallic catalysts and bimetallic catalyst.

Monometallic Ni catalyst and bimetallic catalyst were included altogether two peaks. Besides, the 15%wt.Co/ γ -Al₂O₃ shows peak at 390 °C which were assigned for the reduction of Co₃O₄ to CoO and the step of CoO to Co⁰ was appeared at 600 – 650 °C [29, 31]. Some peaks of 15%wt.Ni/ γ -Al₂O₃ and 1Ni1Co/ γ -Al₂O₃ were observed between 550 and 650 °C which may be attributed to NiO interaction with the support that can be reduced at mild temperature. Also, the peak above 650 °C was ascribed to the reduction of NiAl₂O₄ and interaction of stable NiO phase with the surface [9]. The presence of cobalt hindered the NiAl₂O₄ formation in the bimetallic NiCo catalyst which caused an easier reducibility; in contrast, excessive loaded cobalt metal led to the formation of CoAl₂O₄ the reduction of Co₃O₄ to CoO that was strongly interacted with support and these reason led to decrease a reducibility [29, 32, 33].

4.1.1.4 Ammonia temperature program desorption (NH_3 -TPD)

Desorption curves NH_3 -TPD of 15% wt. Ni/ γ - Al_2O_3 , 1Ni1Co/ γ - Al_2O_3 and 15% wt. Co/ γ - Al_2O_3 are shown in Fig. 4.7. The NH_3 peak of bimetallic catalysts were found within 60 – 350 °C are attributed to weak acid sites. And, Acidity of catalysts was shown in Table 4.2. The bimetallic 1Ni1Co catalyst have acidity lower than both of monometallic catalyst.

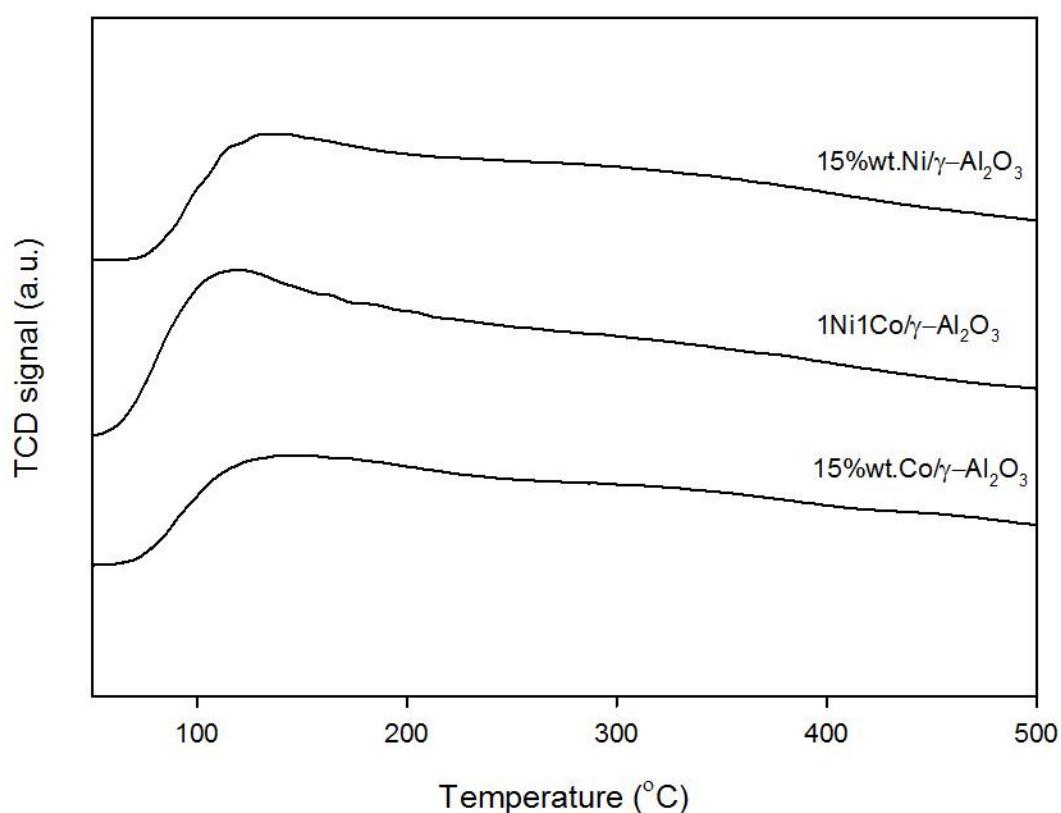


Figure 4.7 NH_3 -TPD profiles of monometallic catalysts and bimetallic catalyst.

Table 4.2 The acidity of catalysts with different molar ratio on alumina supported.

Catalysts	Total acid sites (mmol H^+ /g. cat.)
15%wt.Ni/ γ - Al_2O_3	17.81
7.5%wt.Ni7.5%wt.Co(1Ni1Co)/ γ - Al_2O_3	13.37
15%wt.Co/ γ - Al_2O_3	13.96

4.1.1.5 Carbon monoxide chemisorption (CO-CHEM)

Table 4.3 Dispersion of metal on bimetallic catalysts and active sites.

Catalysts	volume of CO adsorption (cm ³ /g)	% Dispersion	Active sites (*10 ¹⁹ molecule co/g)
15%wt.Ni/ γ -Al ₂ O ₃	0.41	0.7	1.08
1Ni1Co/ γ -Al ₂ O ₃	0.30	0.5	0.71
15%wt.Co/ γ -Al ₂ O ₃	0.21	0.4	0.47

The percent dispersion of metal on catalysts and active sites were investigated amount of carbon monoxide adsorption, the result was shown in Table 4.3. the amount of Co chemisorbed and metal dispersion finds to be related the amount of Ni and Co present in the catalyst. The 15% wt.Ni/ γ -Al₂O₃ have high dispersion of metal and active sites followed by 1Ni1Co/ γ -Al₂O₃ and 15%wt.Co/ γ -Al₂O₃, respectively.

4.1.1.6 Thermo gravimetric and differential thermal analysis (TG-DTA)

The TG-DTA analysis of monometallic 15% wt. Ni/ γ -Al₂O₃, 15% wt. Co/ γ -Al₂O₃ catalyst and bimetallic 1Ni1Co/ γ -Al₂O₃ catalyst after being used in dry reforming of methane were analyzed in Fig. 4.8. The similar trends were detected for 15%wt.Ni/ γ -Al₂O₃ and 1Ni1Co/ γ -Al₂O₃. The 15%wt.Co/ γ -Al₂O₃ had first zone (I) within 50 – 250 °C which caused by disposal of water and substances used in preparation, and second zone for 15%wt.Ni/ γ -Al₂O₃ and 1Ni1Co/ γ -Al₂O₃ were detected. The first zone (I) might be the water between 50 – 250 °C and the second zone (II) between 500 – 680 °C might be removal of physically bonded water and also the disintegration of nitrate compounds[7]. The result showed the coke deposition over 15%wt.Ni/ γ -Al₂O₃ > 15%wt.Co/ γ -Al₂O₃ > 1Ni1Co/ γ -Al₂O₃. The presence of cobalt increased the resistance of coke formation [34, 35]. Also, acidity of catalyst sites appears to be related to amount of carbon deposition[36].

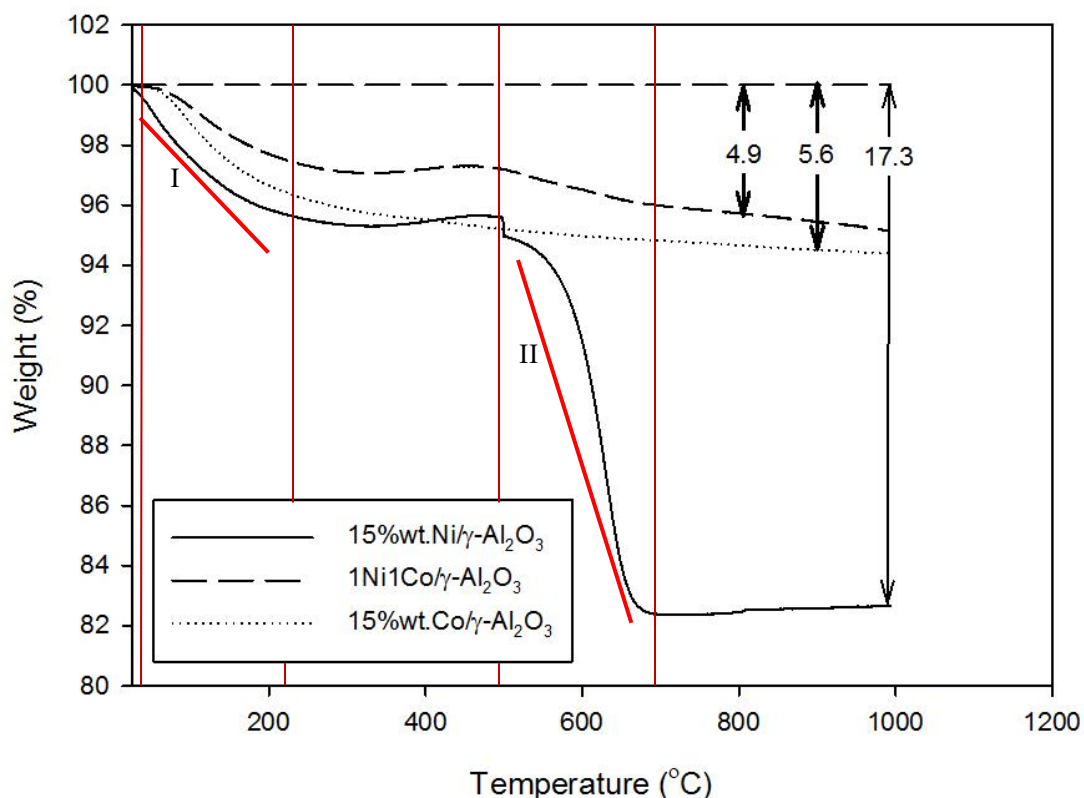


Figure 4.8 TG-DTA analysis of monometallic and bimetallic catalysts after 3 hr. of reaction.

4.1.2 The performance of catalysts

4.1.2.1 The catalytic activity and selectivity

Activity comparison between monometallic catalysts (15% wt. Ni and 15% wt. Co/ γ -Al₂O₃) and bimetallic catalyst (2Ni1Co/ γ -Al₂O₃) in dry reforming of methane were shown in Fig. 4.9. The catalysts were reduced in H₂ ambient at 600 °C for 1 hr. in fixed bed reactor. Then, the reaction was operated to feed CH₄ mixed with CO₂ flow rate 60 mL/min at 700 °C for 1 atm.

The 1Ni1Co/ γ -Al₂O₃ have conversion of CH₄ for 60% and conversion of CO₂ for 66%. Monometallic 15% wt. Ni/ γ -Al₂O₃ have CH₄ conversion for 58% and CO₂ conversion for 65%. The smallest conversion of CH₄ and CO₂ was 15% wt. Co/ γ -Al₂O₃ for 11% and 24%, respectively. All catalysts have similar trend which have more CO₂ conversion than CH₄ conversion which caused by reverse water gas shift reaction. Additionally, the H₂ and CO selectivity of the comparison of monometallic and bimetallic catalysts are shown in Fig. 4.10. The 15% wt. Ni/ γ -Al₂O₃ have the most product H₂ selectivity in this comparison which is 38% which follow by 35% of H₂ selectivity of 1Ni1Co. The metal dispersion appears to be related to the increased methane conversion of catalyst.

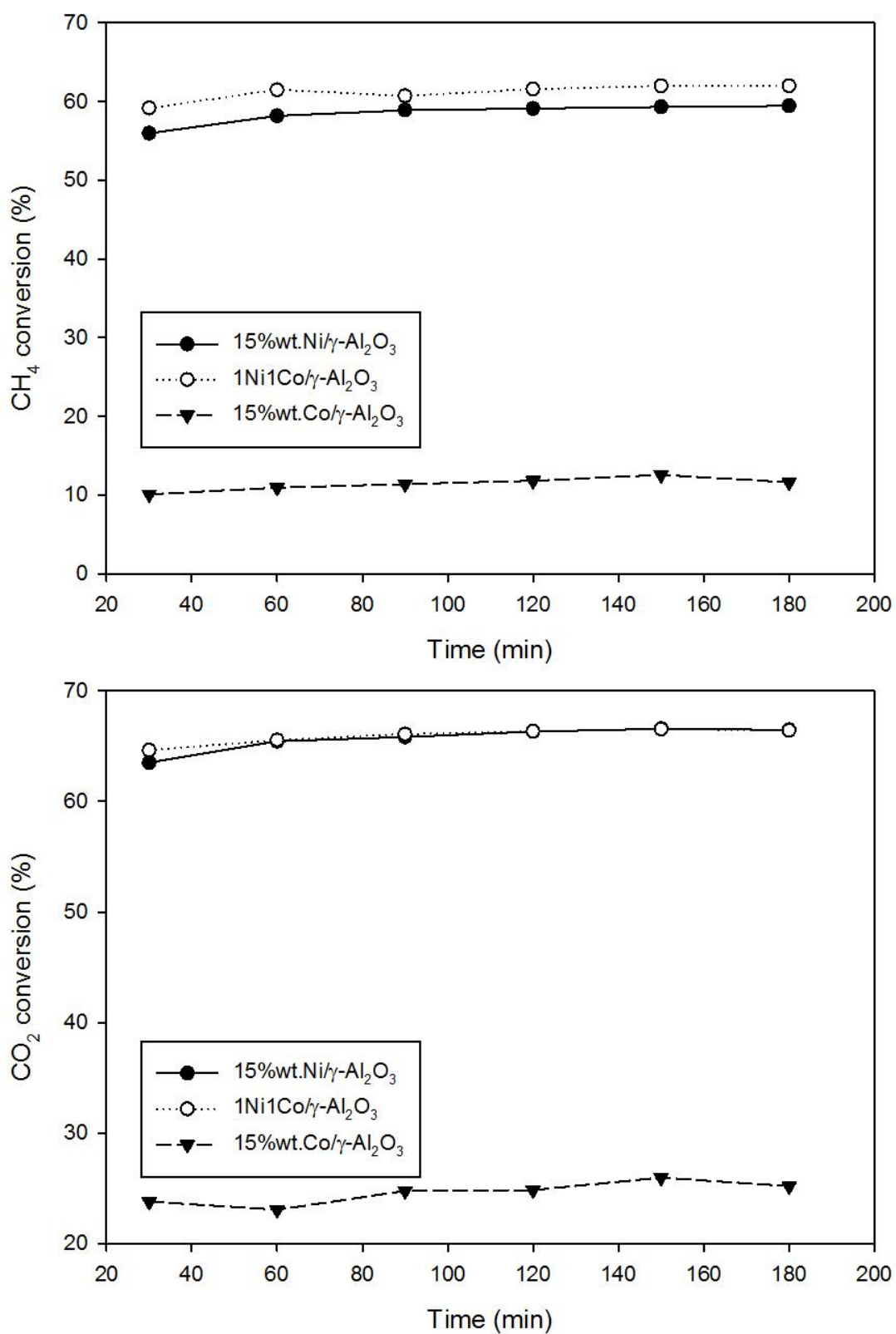


Figure 4.9 The CH₄ and CO₂ conversion of 15%wt.Ni/ γ -Al₂O₃, 1Ni1Co/ γ -Al₂O₃, and 15%wt.Co/ γ -Al₂O₃.

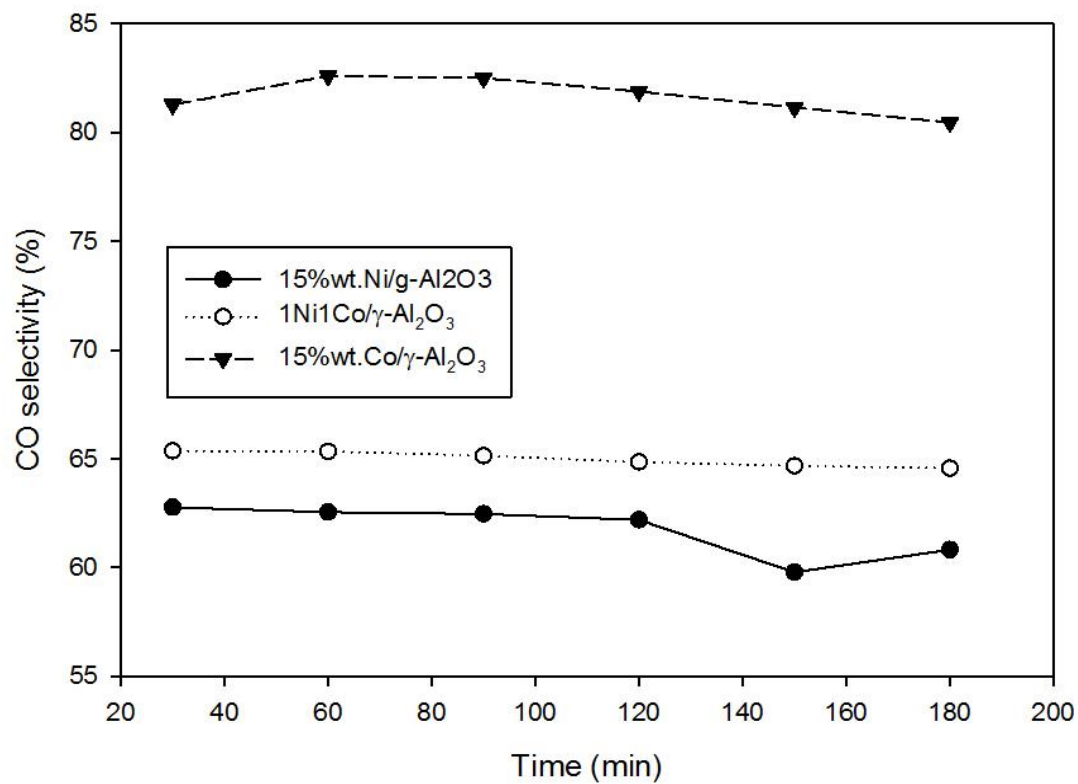
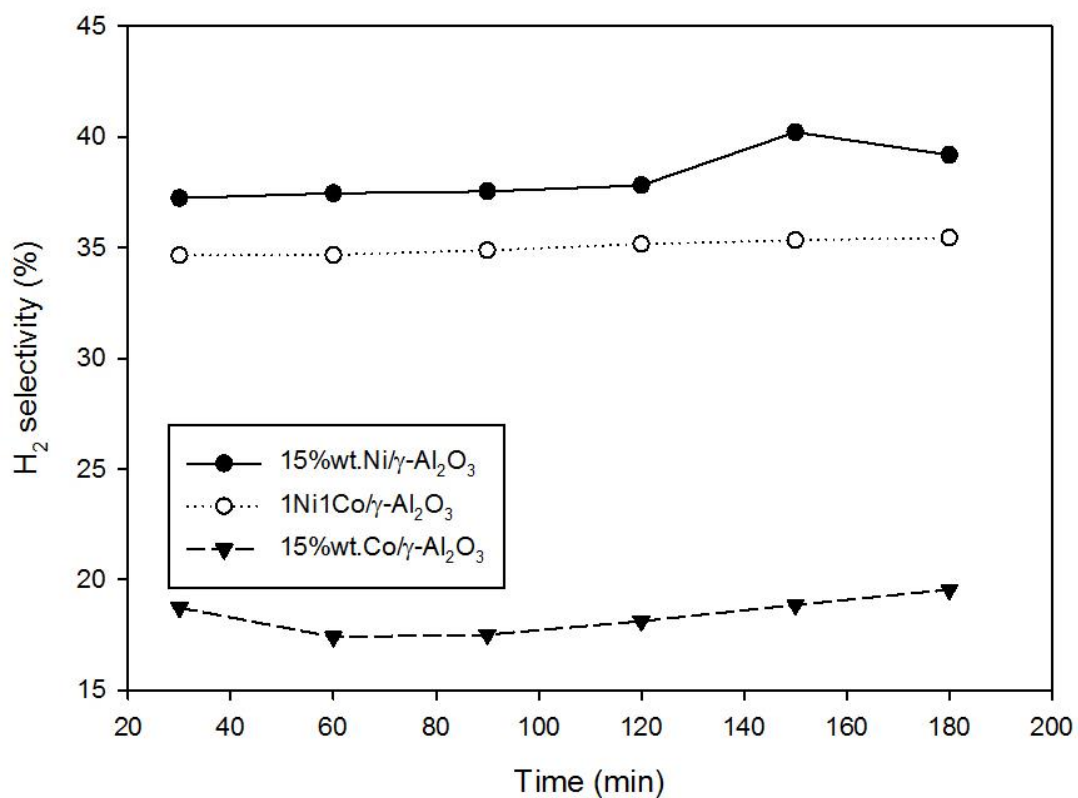


Figure 4.10 The H₂ and CO selectivity of 15%wt.Ni/ γ -Al₂O₃, 1Ni1Co/ γ -Al₂O₃, and 15%wt.Co/ γ -Al₂O₃.

4.2 study of different loading ratios between nickel and cobalt metals

4.2.1 Characterization of catalyst

4.2.1.1 X-Ray Diffraction

The XRD Pattern of bimetallic catalysts to obtain 7.5%wt.Ni7.5%wt.Co/ γ -Al₂O₃ (1Ni:1Co), 10%wt.Ni5%wt.Co/ γ -Al₂O₃ (2Ni:1Co), 11.25%wt.Ni3.75%wt.Co/ γ -Al₂O₃ (3Ni:1Co) indicated in Fig. 4.11. After loading cobalt metal and nickel metal on Al₂O₃ support, the XRD patterns were shown peak of NiO at 37.2°, 43.4°, 63.1° and 37.1°, 45.2° and 65.7° assigned for NiAl₂O₄. The Co₃O₄ or CoAl₂O₄ peaks are observed at 37.2°, 45.1°, 59.6° and 65.7°. The CoO, CoAl₂O₄, NiO and NiAl₂O₄ have no significant different which suggests that those may have similar morphology.

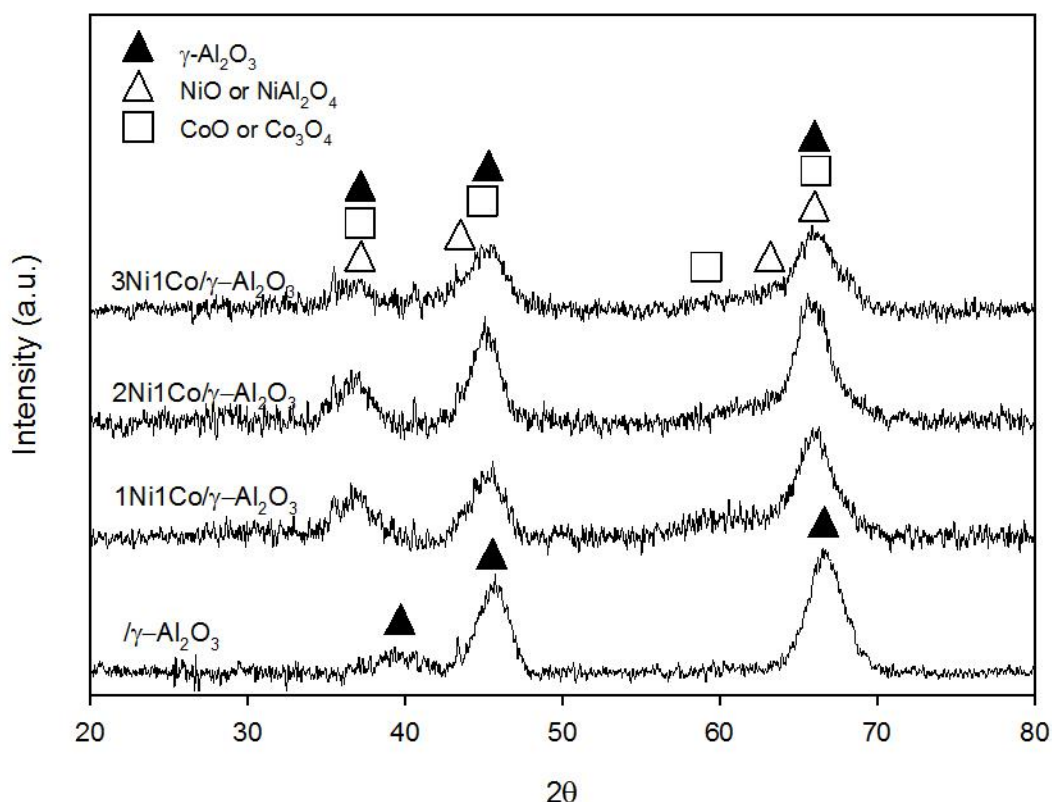


Figure 4.11 XRD pattern of catalysts and support: 3Ni1Co, 2Ni1Co, 1Ni1Co on γ -Al₂O₃ and γ -Al₂O₃.

4.2.1.2 Nitrogen adsorption-desorption

The specific surface areas of calcined support and the different bimetallic loading content catalysts were measured using the Brunauer-Emmitt-Teller Method (BET). BET surface area, pore volume, and pore size of bimetallic (1Ni1Co, 2Ni1Co and 3Ni1Co) on Al₂O₃ catalysts were summarized in Table 4.4. The surface areas of bimetallic catalysts were slightly less than the alumina support. This suggests that the loaded Ni and Co metal particle may blocked some pore of alumina support. The 3Ni1Co/ γ -Al₂O₃ has higher specific surface area than 2Ni1Co/ γ -Al₂O₃ and 1Ni1Co/ γ -Al₂O₃, respectively.

Table 4.4 BET surface areas, pore volume, pore size and dispersion of monometallic and bimetallic on γ -Al₂O₃ catalysts.

Catalyst	BET surface area (m ² /g)	Average pore diameter (nm) ^a	Pore volume (cm ³ (STP)/g) ^a
γ -Al ₂ O ₃	189	2.9	0.2
7.5Ni7.5Co/ γ -Al ₂ O ₃ (1Ni1Co)	176	3.1	0.2
10Ni5Co/ γ -Al ₂ O ₃ (2Ni1Co)	182	3.0	0.21
11.25Ni3.75Co/ γ -Al ₂ O ₃ (3Ni1Co)	185	3.2	0.2

^aCalculated from BJH model.

The N₂ adsorption-desorption isotherm of the different loading contents of bimetallic catalysts are showed in Fig. 4.12. All bimetallic catalysts can be assigned as a type IV which attributed for micro-mesoporous materials. The H2 type adsorption hysteresis are involved with a consequence of the interconnectivity of pores. In such systems, the distribution of pore sizes and the pore shape is not well-defined or irregular.

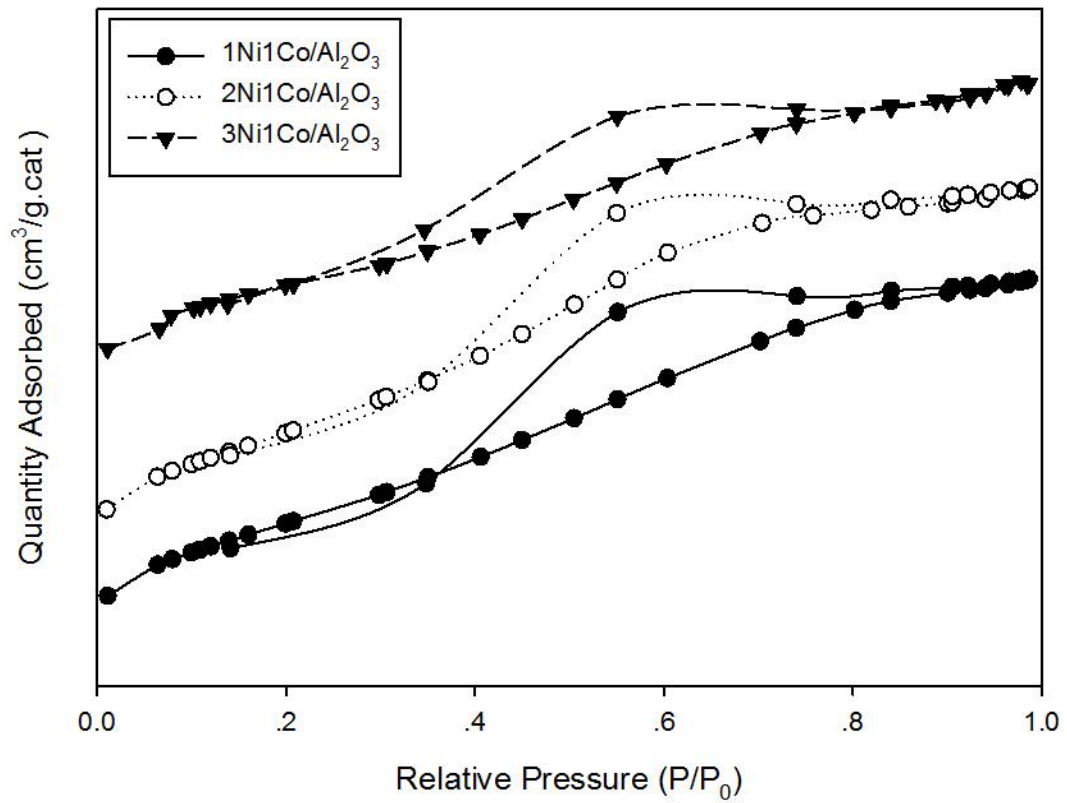


Figure 4.12 The nitrogen adsorption/desorption isotherms of catalysts.

4.2.1.3 Scanning Electron Microscopy (SEM-EDX)

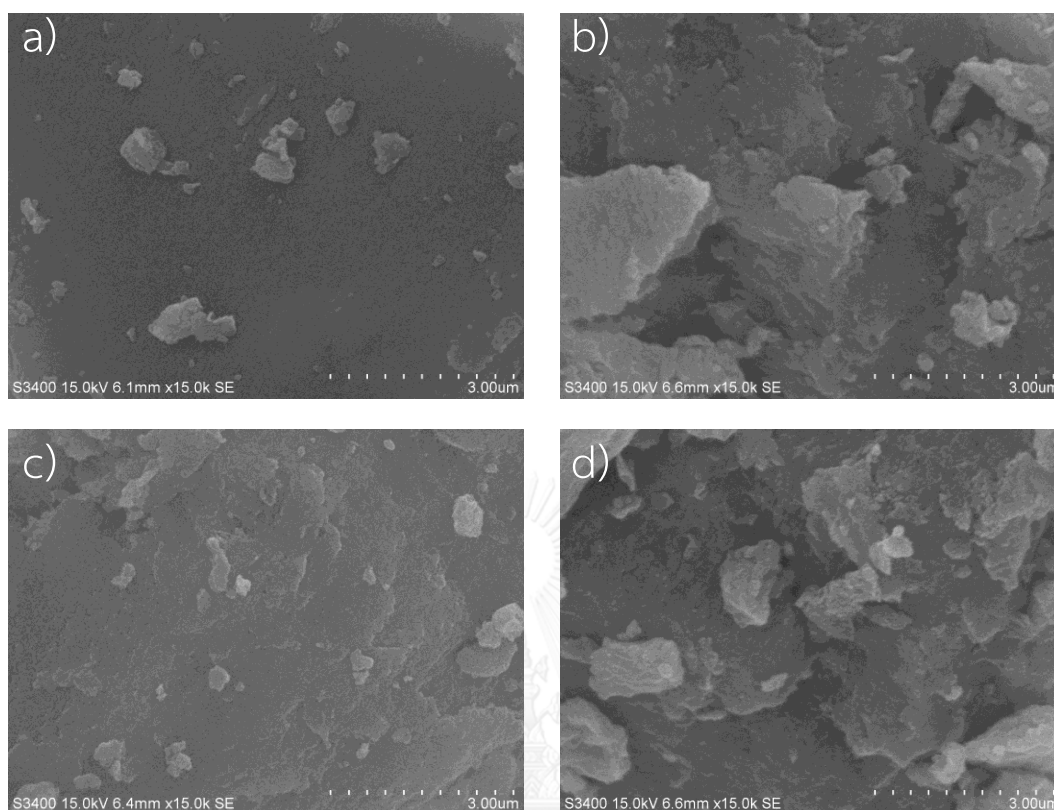


Figure 4.13 The SEM images of the (a) γ - Al_2O_3 , (b) $3\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$ and (c) $2\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$ and (d) $1\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$.

The morphology of $\gamma\text{-Al}_2\text{O}_3$, $3\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$, $2\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$ and $1\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$ were shown in Fig. 4.13. The bimetallic catalyst had no significantly differ with the support that the crystallinity of the supports which suggests that is not affected by NiO and CoO loading. So, the catalyst morphology is similar to Al_2O_3 support.

4.2.1.4 Hydrogen temperature program reduction (H_2 -TPR)

Hydrogen temperature - programmed reduction (H_2 -TPR) were conducted to investigate the reducibility of the catalysts. The TPR profiles are reported in Fig. 4.14

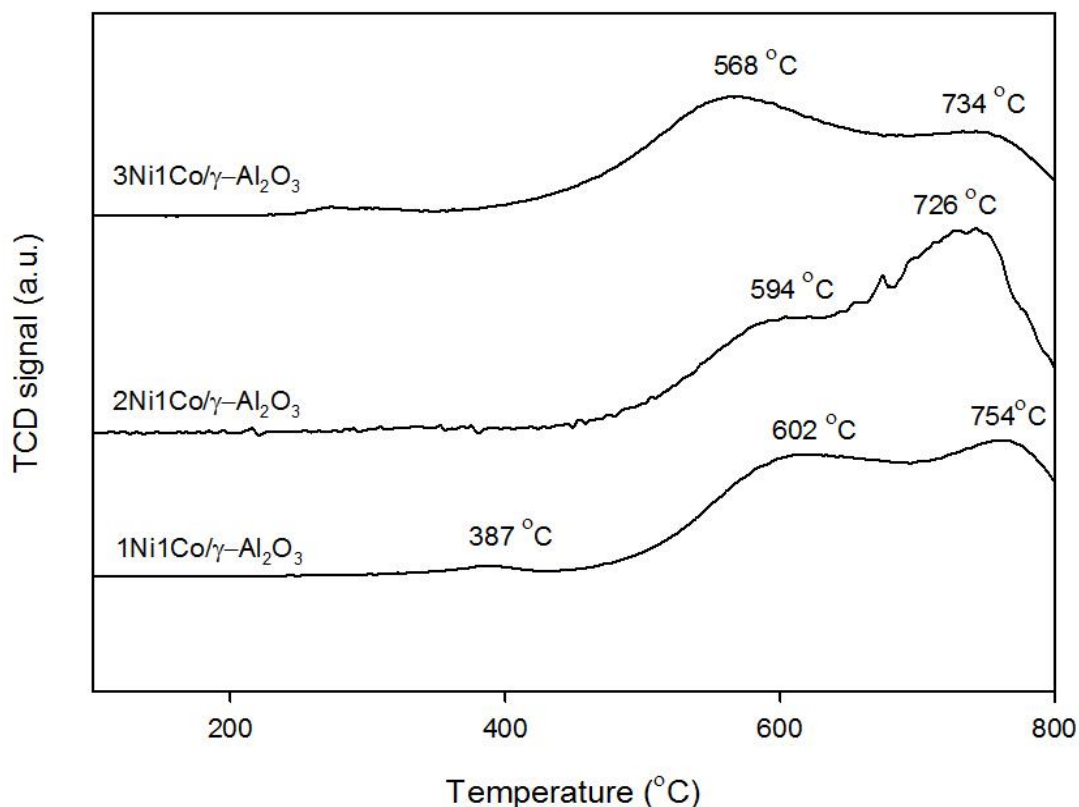


Figure 4.14 The TPR profiles of the different loading ratios between Nickel and Cobalt on Al₂O₃ support.

All bimetallic catalysts were included altogether two peaks. Some peaks were observed between 550 and 650 °C which may be attributed to NiO interaction with the support that can be reduced at mild temperature. Also, the peak above 650 °C was ascribed to the reduction of NiAl₂O₄ and strong interaction of NiO with the surface and also assigned to the reduction of mixed metal-support oxides. The 1Ni1Co/ γ -Al₂O₃ shows small peak at 390 °C which were assigned for the reduction of Co₃O₄ to CoO and while the second reduction step of CoO to Co⁰ was appeared at 600 – 650 °C.. Although, the presence of cobalt hindered the NiAl₂O₄ formation in the bimetallic NiCo catalyst which caused an easier reducibility; in contrast, excessive loaded cobalt metal leaded to the formation of CoAl₂O₄ the reduction of Co₃O₄ to CoO that was strongly interacted with support and these reason lead to decrease a reducibility[29, 32, 33].

4.2.1.5 Ammonia temperature program desorption (NH_3 -TPD)

Ammonia temperature program desorption was a technique to measure the acidity on catalyst surfaces. The desorption curves NH_3 -TPD of $1\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$, $2\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$ and $3\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$ are shown in Fig. 4.15. The NH_3 peak of bimetallic catalysts were found within 60 – 350 °C are attributed to weak acid sites.

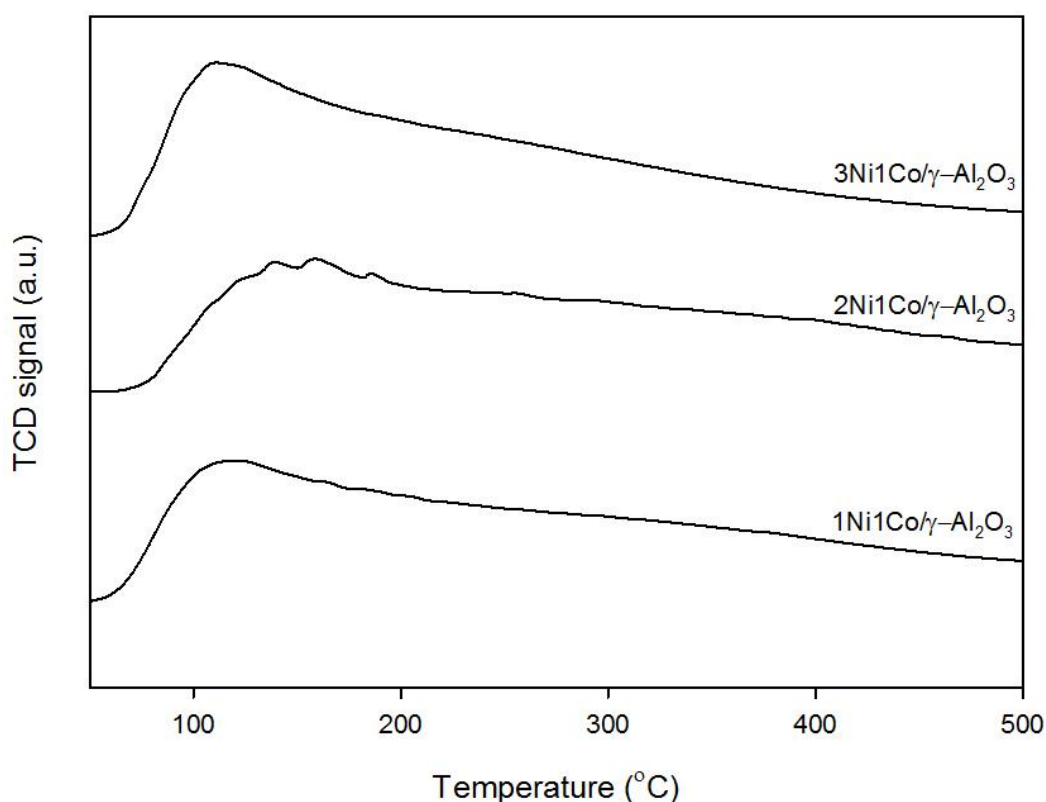


Figure 4.15 The NH_3 -TPD profiles of the bimetallic catalysts.

In addition, the amounts of acid sites on the surface catalysts show in table 4.5. The acidity of bimetallic catalysts $3\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$ have higher acidity than $2\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$ and $1\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$ catalysts.

Table 4.5 The acidity of catalysts with different molar ratio on alumina supported.

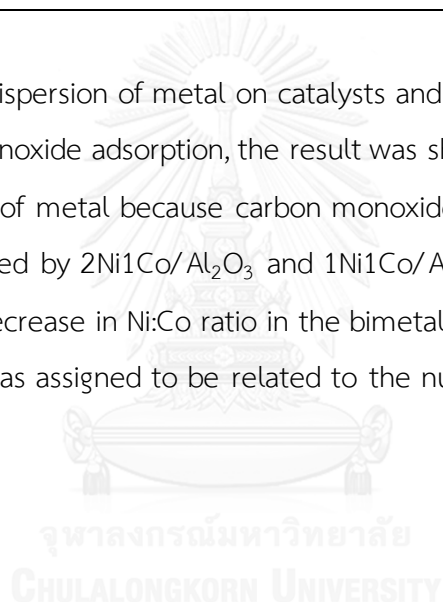
Catalysts	Total acid sites (mmol H^+ /g. cat.)
$1\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$	13.37
$2\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$	13.54
$3\text{Ni}1\text{Co}/\gamma\text{-Al}_2\text{O}_3$	14.18

4.2.1.6 Carbon monoxide chemisorption (CO-CHEM)

Table 4.6 Dispersion of metal on bimetallic catalysts and active sites.

Catalysts	volume of CO		Active sites (*10 ¹⁹ molecule co/g)
	adsorption (cm ³ /g)	% Dispersion	
1Ni1Co/ γ -Al ₂ O ₃	0.30	0.5	0.71
2Ni1Co/ γ -Al ₂ O ₃	0.33	0.6	0.78
3Ni1Co/ γ -Al ₂ O ₃	0.52	0.9	1.37

The percent dispersion of metal on catalysts and active sites were investigated amount of carbon monoxide adsorption, the result was shown in Table 4.6. The 3Ni1Co have good dispersion of metal because carbon monoxide was high adsorbed and high active site and followed by 2Ni1Co/Al₂O₃ and 1Ni1Co/Al₂O₃. the volume of adsorbed CO decreased with decrease in Ni:Co ratio in the bimetallic NiCo catalysts. The amount of metal dispersion was assigned to be related to the number of active metal sites.



4.2.1.7 Thermo gravimetric and differential thermal analysis (TG-DTA)

This technique was used to determine amount of coke or deposited carbon. The TG-DTA analysis of different molar ratio content between Ni and Co on alumina support after being used in dry reforming of methane were demonstrated in Fig. 4.16. The similar trends were detected for 1Ni1Co/ γ -Al₂O₃, 2Ni1Co/ γ -Al₂O₃ and 3Ni1Co/ γ -Al₂O₃ catalysts. The first zone (I) which might be the water between 50 – 250 °C and the second zone (II) between 500 – 680 °C which might be removal of carbon deposition on surface catalysts. 3Ni1Co/ γ -Al₂O₃ had the highest amount of weight loss, followed by 2Ni1Co/ γ -Al₂O₃ and 1Ni1Co/ γ -Al₂O₃, respectively[7]. Therefore, the highest amount of carbon deposition was presented on the 3Ni1Co/ γ -Al₂O₃.

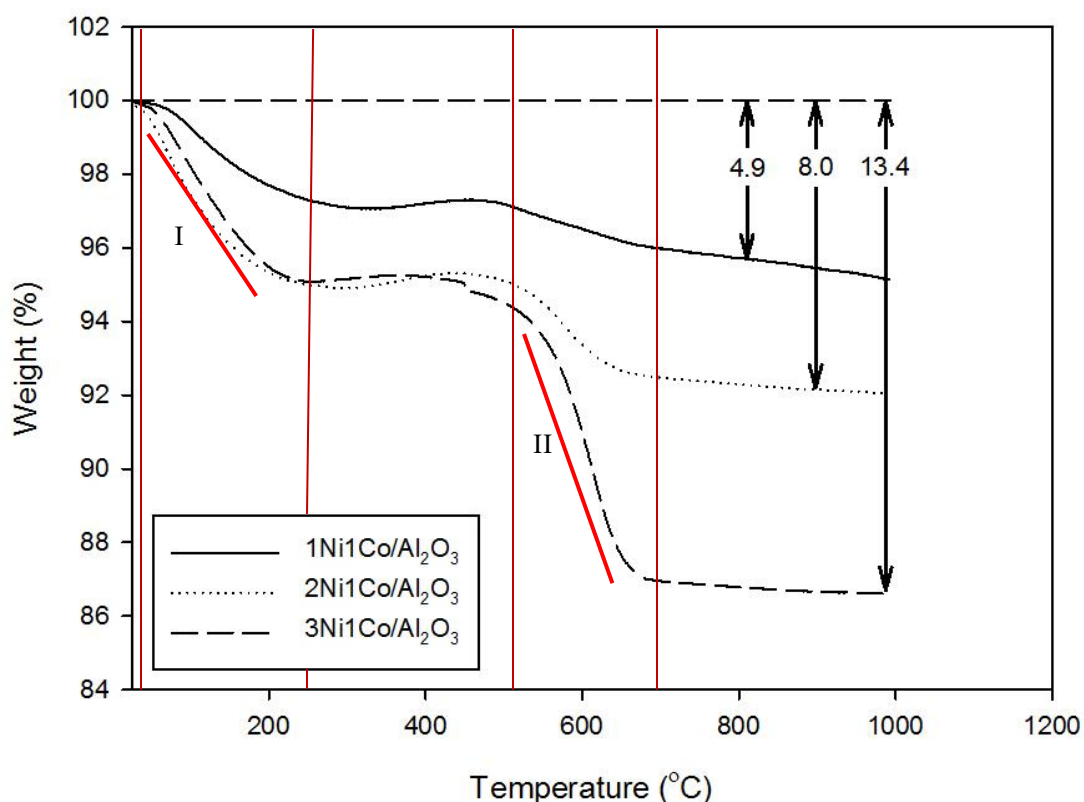


Figure 4.16 TG-DTA analysis of different molar ratio loading of bimetallic after 3 hr. of reaction.

4.2.2 The performance of catalyst

4.2.2.1 The catalytic activity and selectivity

The activities of bimetallic catalysts (1Ni1Co/ γ -Al₂O₃, 2Ni1Co/ γ -Al₂O₃ and 3Ni1Co/ γ -Al₂O₃) were studied in dry reforming of methane.

The CH₄ and CO₂ conversion were shown in Fig. 4.17. The CH₄ conversion of 3Ni1Co/ γ -Al₂O₃, 2Ni1Co/ γ -Al₂O₃, and 1Ni1Co/ γ -Al₂O₃ are approximately 74%, 70%, and 60%, respectively. In term of CO₂ conversion, the performance of 3Ni1Co/ γ -Al₂O₃, 2Ni1Co/ γ -Al₂O₃, and 1Ni1Co/ γ -Al₂O₃ are 79%, 74% and 66%. The higher CO₂ conversion is due to reverse water gas shift (RWGS). Reverse Boudouard reaction could also be effective on product selectivity[36, 37]. The selectivity of H₂ and CO were presented in Fig. 4.18. The H₂ selectivity of 3Ni1Co/ γ -Al₂O₃, 2Ni1Co/ γ -Al₂O₃, and 1Ni1Co/ γ -Al₂O₃ are 41%, 40% and 35%. And, for the CO selectivity are 59%, 60% and 65%, respectively. The 3Ni1Co/ γ -Al₂O₃ was the most efficiency in the reaction. Addition to 3Ni1Co/ γ -Al₂O₃, the high activity was affected by increasing of metal dispersion and surface area[2, 6, 9, 38, 39].

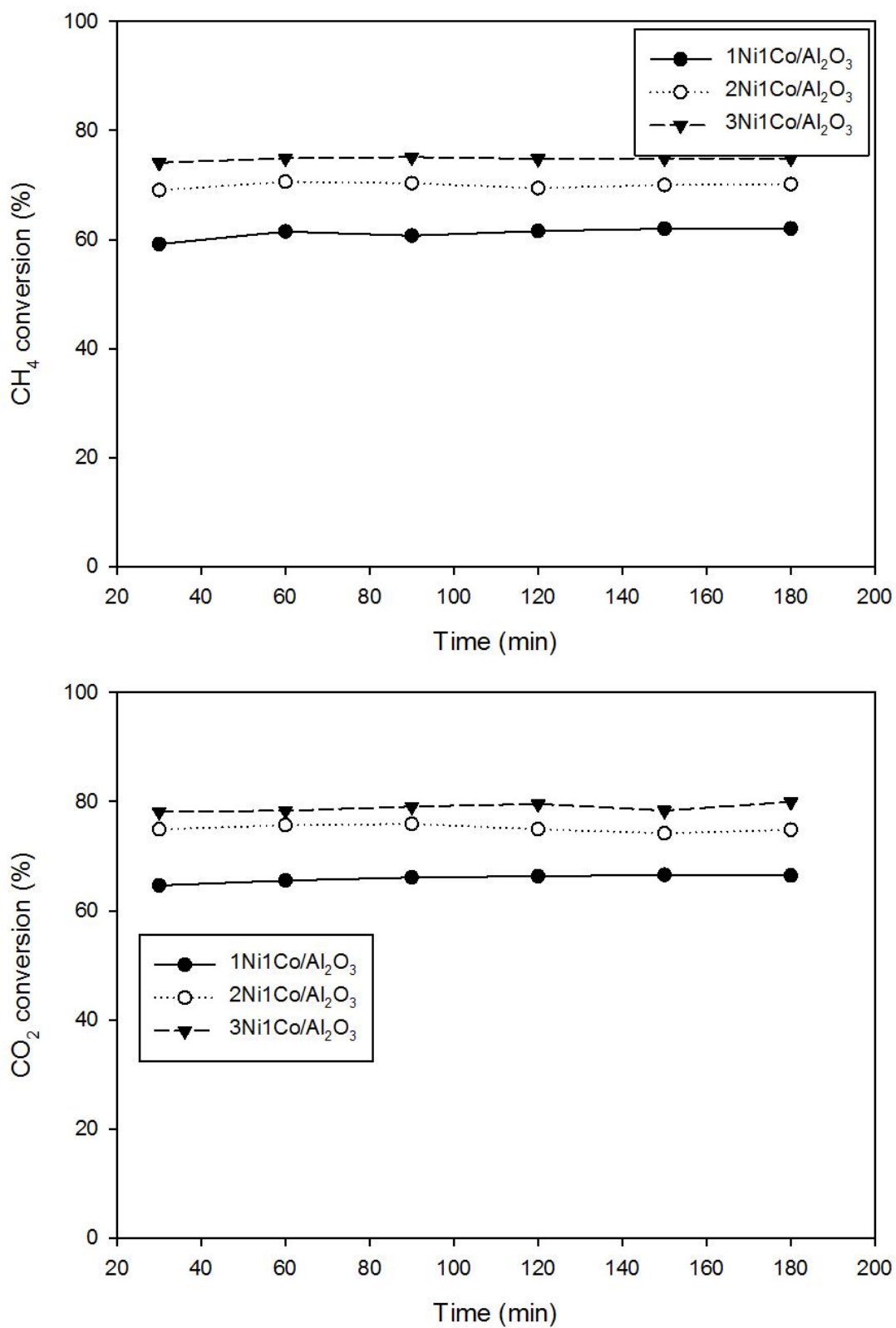


Figure 4.17 The CH₄ and CO₂ conversion of 3Ni1Co/ γ -Al₂O₃, 2Ni1Co/ γ -Al₂O₃, and 1Ni1Co/ γ -Al₂O₃.

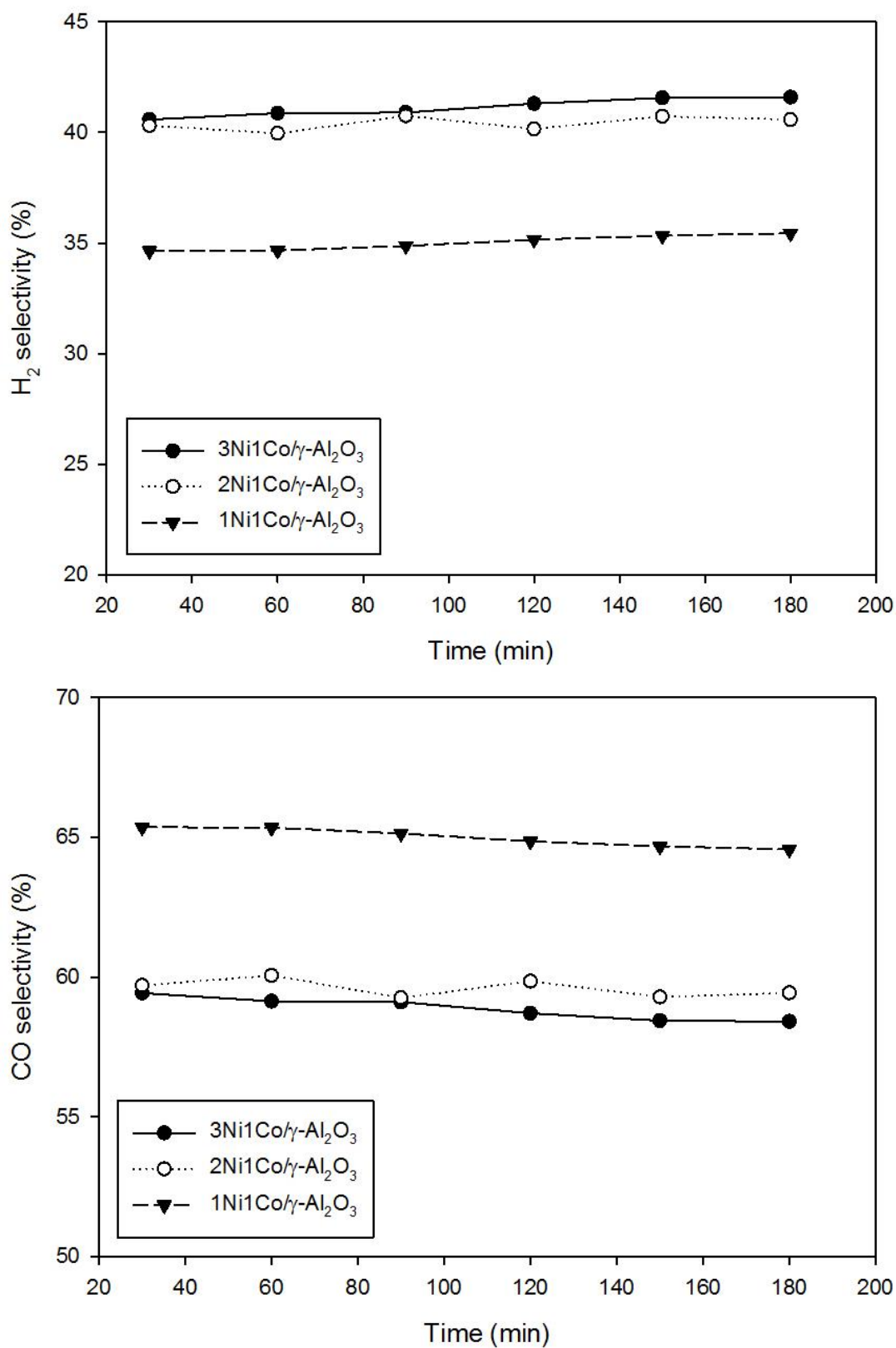


Figure 4.18 The H₂ and CO selectivity of 3Ni1Co/γ-Al₂O₃, 2Ni1Co/γ-Al₂O₃, and 1Ni1Co/γ-Al₂O₃.

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

The CO₂ reforming of methane reaction was studied over NiCo/Al₂O₃, Ni/Al₂O₃ and Co/Al₂O₃. The presence of cobalt in the bimetallic catalysts improved the metal dispersion and specific surface area. Furthermore, cobalt metal decreased carbon formation on catalyst surface. The bimetallic catalysts (3Ni1Co/Al₂O₃) exhibited the highest performance on the reaction which had high activity including; 74% of CH₄ conversion, 79% of CO₂ conversion, 41% of H₂ selectivity, high metal dispersion and high specific surface area. Although, the 3Ni1Co most suffered from carbon formation but 3Ni1Co had the acceptable amount of carbon deposition and can be properly used for long term.

5.2 Recommendations

From this study, recommendations are as follows by:

To improve the resistance of coke formation on 3Ni1Co/Al₂O₃ catalyst in the CO₂ reforming of methane for commercial applications such as using mixed support of ZrO₃ and Al₂O₃ as ZrO₃ actives with CO₂ interaction.

To determine amount of elements metals by using inductively coupled plasma (ICP).

To study about the co-precipitation for preparation of catalyst which can improve metal dispersion since metal dispersion mainly contributes for the high activity in CO₂ reforming of methane.

To characterize the used catalyst with scanning electron microscopy for observation of the carbonaceous species on the catalyst surface.

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APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

1. Preparation of 15%wt.Ni / γ -Al₂O₃ monometallic catalyst by Sol-gel

Example: preparation of Al₂O₃

Reagent Alumina iso propoxide = 6 g
 DI Water = 80 ml
 Ethanol = 80 ml
 Finally Al₂O₃ after calcination process = 1.3986 g as 85%wt of catalyst and 15%wt for metal.

Ni(NO₃)₂.6H₂O, Molecular weight = 292 g/mol

Ni, Molecular weight = 59 g/mol

Calculation

15% of Ni = $15 \times 1.3986 / 85$ = 0.2468 g

For amount of nickel in preparation;

Ni = $(0.2468 \times 292) / 59$ = 1.2215 g

The 15%wt.Ni/Al₂O₃ catalyst was prepared from the 1.2215 g of Ni(NO₃)₂.6H₂O for sol-gel method.

2. Preparation of Ni-Co/ γ -Al₂O₃ bimetallic catalyst by Sol-gel

Preparation of 7.5%Ni7.5%Co/Al₂O₃ bimetallic catalysts by Sol-gel method

Example: Preparation of bimetallic catalyst.

Reagent Ni(NO₃)₂·6H₂O, Molecular weight = 292 g/mol

Ni, Molecular weight = 59 g/mol

Co(NO₃)₂·6H₂O, Molecular weight = 292 g/mol

Co, Molecular weight = 59 g/mol

Basis; Al₂O₃ 1.3986 g catalyst, consisted of: Alumina = 85%

Nickel = 7.5 %

Cobalt = 7.5 %

Calculation

$$7.5\% \text{ of Ni and Co} = 7.5 \times 1.3986 / 85 = 0.1234 \text{ g}$$

For amount of nickel and cobalt in preparation;

$$\text{Ni, Co} = (0.1234 \times 292) / 59 = 0.6108 \text{ g}$$

The 7.5%Ni7.5%Co/Al₂O₃ catalyst was prepared from the 0.6108 g of Ni(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O for sol-gel method.

APPENDIX B

CALIBRATION CURVES

The calibration curves are used to calculate composition of products and reactants in carbon dioxide reforming of methane. The calculation curves were shown in this appendix.

The Thermal Conductivity Detector (TCD), gas chromatography Shimadzu model 8A was used to analyze the concentration of products and reactants by using molecular sieve 5A and porapack-Q column.

Mole of reagent in y-axis and area reported by gas chromatography in x-axis are exhibited in the curves. The calibration curves of methane, carbon dioxide, hydrogen and carbon monoxide are illustrated in Figure C1-C4, respectively.

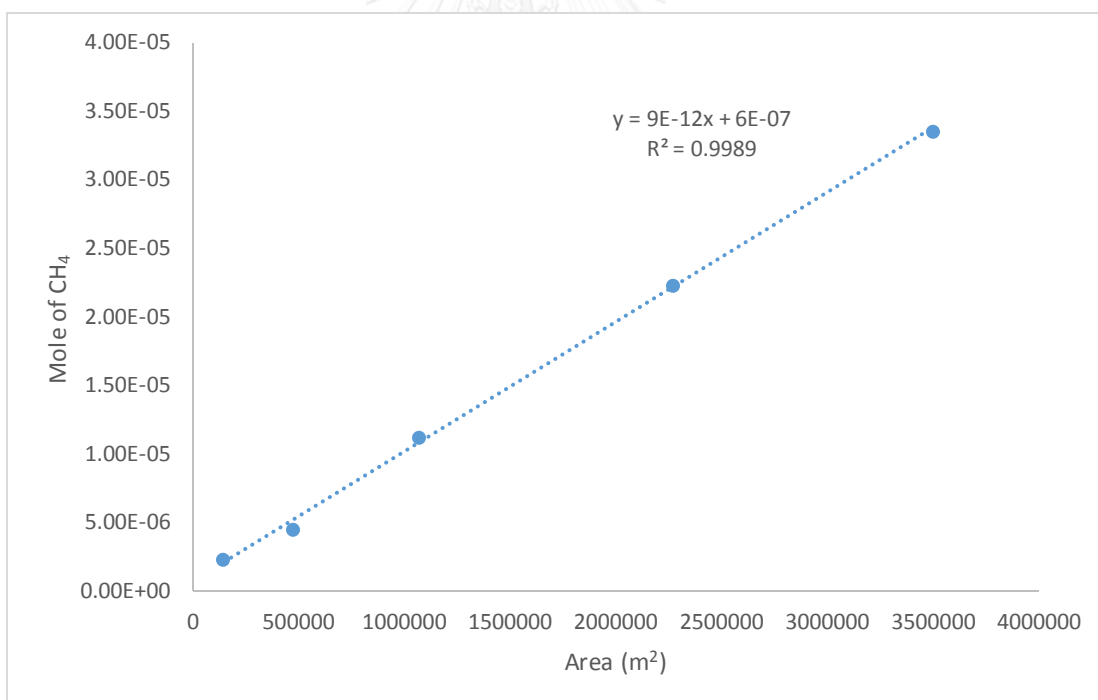


Figure B1 The calibration curve of methane.

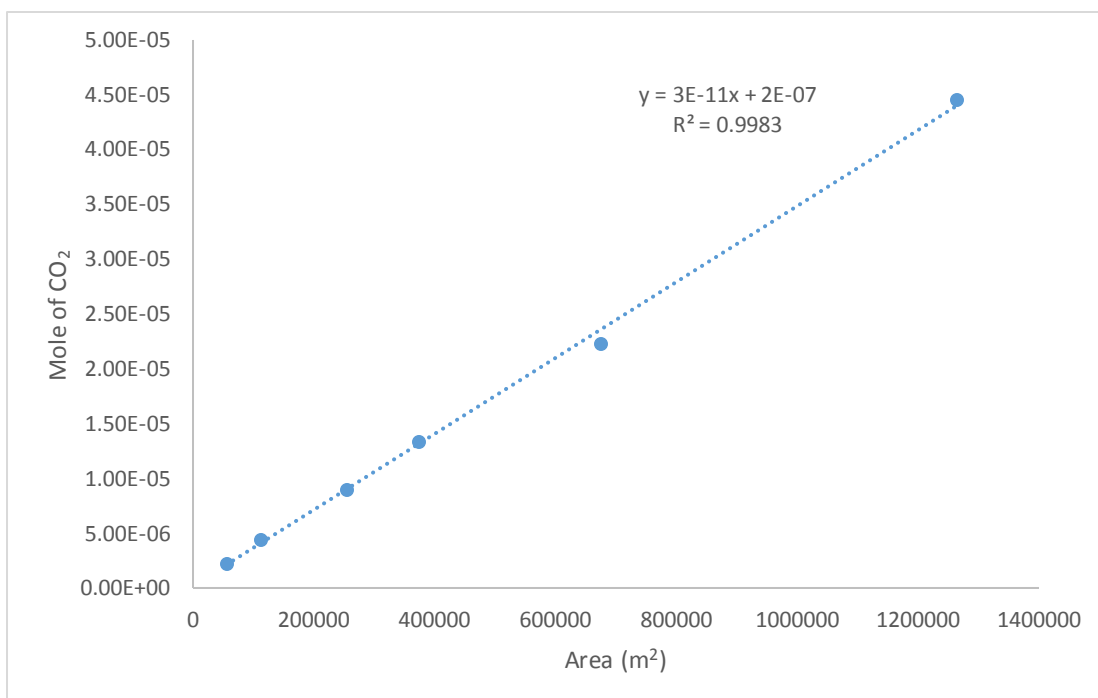


Figure B2 The calibration curve of carbon dioxide.

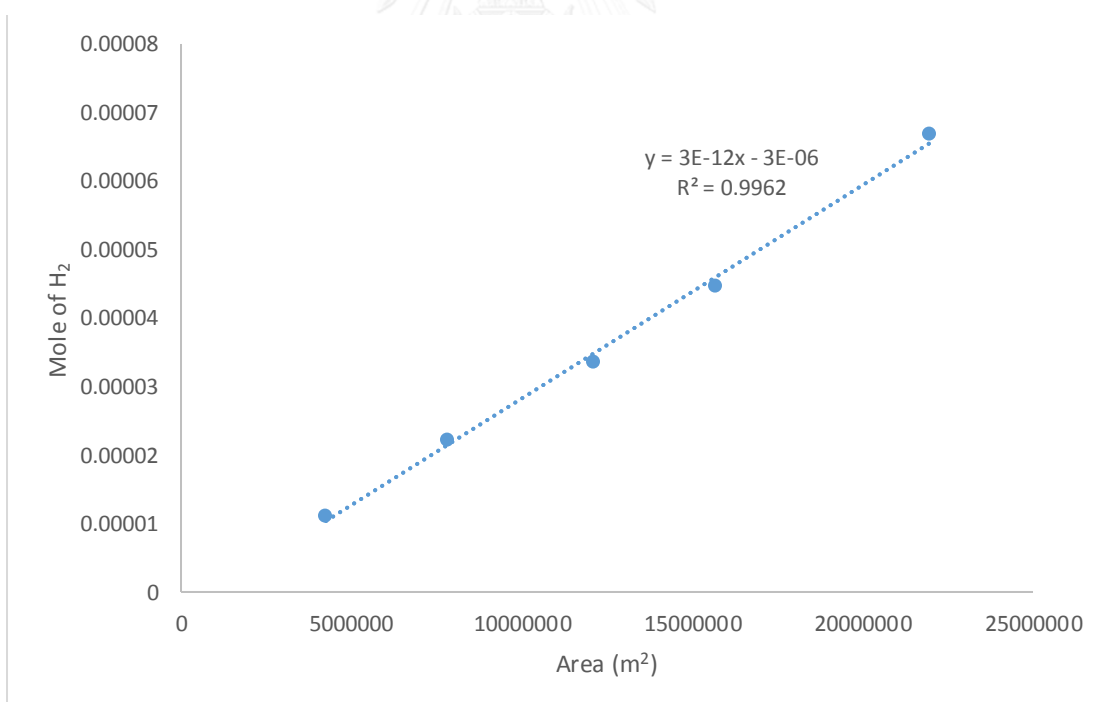


Figure B3 the calibration curve of hydrogen.

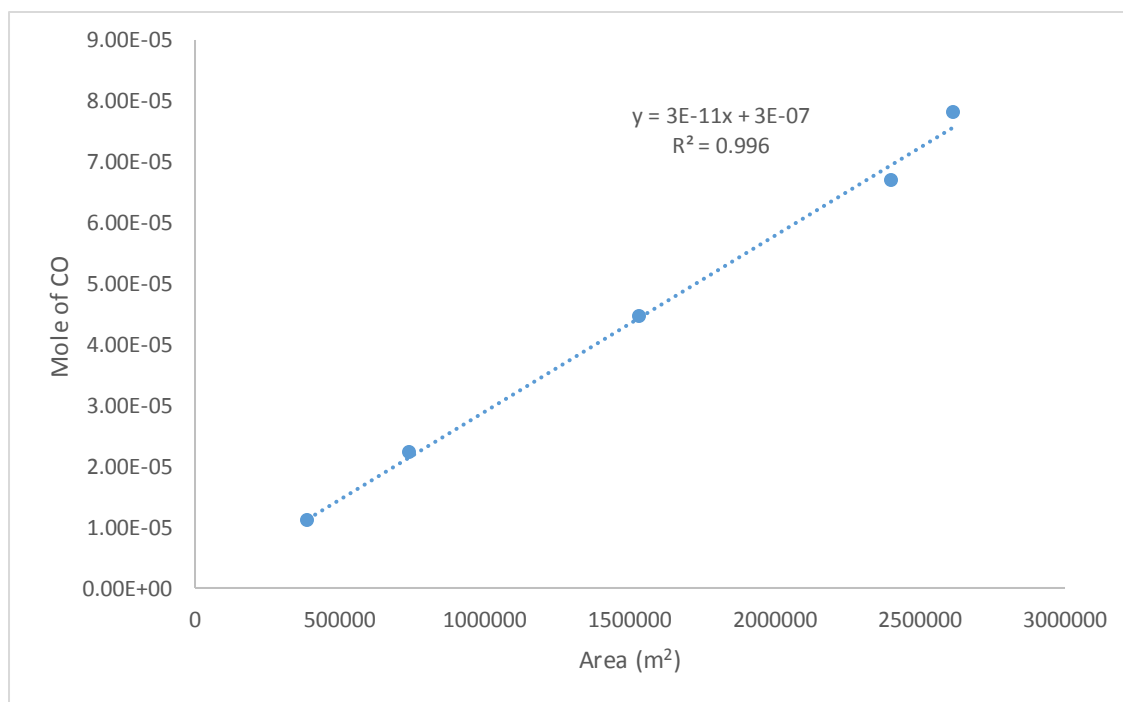
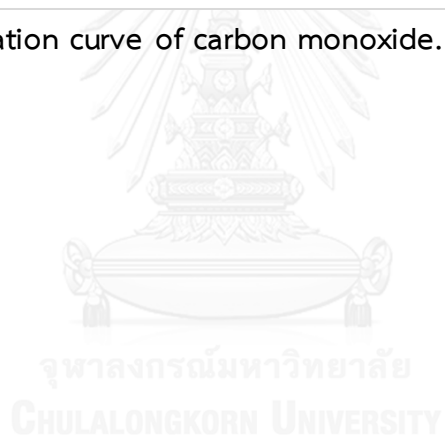


Figure B4 The calibration curve of carbon monoxide.



APPENDIX C

DATA FOR CALCULATION OF ACID SITE

The total acid sites are measured by NH₃-TCD technique.

Calculation

77.57016 ml/area unit is conversion of Micrometrics Chemisorb 2750. Therefore, total peak volume is derived from

Example;

10%Ni5%Co/ γ -Al₂O₃ has total peak area of 4.91

Total peak volume = 77.57016 × 4.91

= 380.9 ml

Adsorbed volume of 15% NH₃ = 0.15 × Total peak volume

= 57.135 ml

Equation to calculate total acid sites;

$$\text{Total acid sites} = \frac{(77.57016)(\text{total peak volume,ml})(101.325,\text{Pa})}{(8.314 \text{ Pa.m}^3/\text{K.mmol})(298 \text{ K})(\text{weight of catalyst,g})}$$

Total acid sites = 23.32 mmol H⁺/g

APPENDIX D

CALCULATION FOR METAL ACTIVE SITES AND DISPERSION

Calculation of the total CO chemisorption and metal dispersion of the catalyst, a stoichiometry of CO/Ni = 1 and CO/Co = 1. The calculation procedure is as follows:

Example: Calculation of the total CO chemisorption of 15%Ni/ γ -Al₂O₃

Variable	Value
S _f =stoichiometry factor CO:Ni	1
V _{ads} =volume adsorbed	0.46 cm ³ /g
V _g = molar volume of gas at STP	22414 cm ³ /mol
m.w. =molecular weight of metal (Ni)	59 g/mol
%M =%metal	15%
V _{injet} =volume injected	= 0.02 cm ³
M =mass of sample = 0.1 g	0.1021 g

$$\begin{aligned} \% \text{ Metal Dispersion (\%D)} &= S_f \times \frac{V_{\text{ads}}}{V_g} \times \frac{\text{m.w.}}{\%M} \times 100\% \times 100\% \\ &= 0.8 \% \end{aligned}$$

$$\begin{aligned} \text{Active site (molecule of CO/g)} &= S_f \times \frac{V_{\text{ads}}}{V_g} \times 6.02 \times 10^{23} \\ \text{So} \qquad \qquad \qquad &= 1.23 \quad \text{molecule of CO/g} \end{aligned}$$

APPENDIX E

CALCULATION FOR CONVERSION SELECTIVITY AND YIELD

The conversions of CO₂ and CH₄ are defined in Equation (E.1) and (E.2) and the selectivity of H₂ and CO are defined in Equation (E.3) and (E.4), respectively

$$\text{CH}_4 \text{ conversion} = \frac{(\text{CH}_{4\text{in}}) - (\text{CH}_{4\text{out}})}{\text{CH}_{4\text{in}}} \times 100 \quad \text{Eq (E.1)}$$

$$\text{CO}_2 \text{ conversion} = \frac{(\text{CO}_{2\text{in}}) - (\text{CO}_{2\text{out}})}{\text{CO}_{2\text{in}}} \times 100 \quad \text{Eq (E.2)}$$

$$\text{H}_2 \text{ selectivity} = \frac{(\text{H}_{2\text{in}}) - (\text{H}_{2\text{out}})}{\text{H}_{2\text{in}}} \times 100 \quad \text{Eq (E.3)}$$

$$\text{CO selectivity} = \frac{(\text{CO}_{\text{in}}) - (\text{CO}_{\text{out}})}{\text{CO}_{\text{in}}} \times 100 \quad \text{Eq (E.4)}$$

VITA

Mr. Supawat Pachop was born on March 27th, 1992 in Ubonratchathani, Thailand. She finished high school from Satri Wat Rakhang School in 2010, and received the bachelor's degree of Chemical Engineering from Faculty of Engineer, Khon kaen University in 2014. She continued her master's study at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in June, 2015.

